APR 9 4 1933

U. S. DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS JOURNAL OF RESEARCH

Vol. 10 FEBRUARY, 1933 No. 2

CONTENTS

RP. No.	TITLE AND AUTHOR	Page
522.	The elimination of background "noise" in sensitive pulse amplifiers. L. F. Curtiss	151
523.	The pressure of saturated water vapor in the range 100° to 374° C. N. S. Osborne, H. F. Stimson, E. F. Fiock, and D. C. Ginnings	155
524.	Some fusion properties of ground coat enamels as influenced by composition. W. N. Harrison and B. J. Sweo	189
525.	The photographic emulsion: The mechanism of hypersensitization. Burt H. Carroll and Donald Hubbard	211
526.	Temperature effect and its elimination in Geiger-Müller tube counters. L. F. Curtiss	229
527.	Operation of thick-walled X-ray tubes on rectified potentials. Lauriston S. Taylor and C. F. Stoneburner	233
528.	Apparatus for comparison of length of gages. Charles Moon	249
529.	Clay in concrete. D. A. Parsons	257
530.	Reference tables for platinum to platinum-rhodium thermocouples. Wm. F. Roeser and H. T. Wensel	275

BUREAU OF STANDARDS JOURNAL OF RESEARCH

CONTENTS OF RECENT NUMBERS

August, 1932 (Vol. 9, No. 2)

RP461. A vacuum tube amplifier for feeble pulses. L. F. Curtiss. Price 5 cents.
RP462. Infra-red spectra of helium. William F. Meggers and G. H. Dieke. Price 5 cents.
RP463. Tests of cellular sheet-steel flooring. J. M. Frankland and H. L. Whittemore. Price 10 cents.
RP464. The influence of temperature on the evolution of hydrogen sulphide from vulcanized rubber. A. D. Cummings. Price 5 cents.
RP465. Some of the factors which affect the measurement of sound absorption. V. L. Chrisler and Catherine E. Miller. Price 5 cents.
RP466. The reciprocal spherical aberration of an optical system including higher orders. Harold F. Bennett. Price 5 cents.
RP467. An attachment for turning approximately spherical surfaces of small curvature on a lathe. I. C. Gardner. Price 5 cents.
RP468. Wave lengths and Zeeman effects in lanthanum spectra. William F. Meggers. Price 5 cents.
RP469. Note on the freezing point of "iso-octane" 2, 2, 4-trimethylpentane. Johannes H. Bruun and Mildred M. Hicks-Bruun. Price 5 cents.
RP470. A twin-bomb method for the accurate determination of pressure-volume-temperature data and a simple method for the accurate measurement of high pressure. Edward W. Washburn. Price 5 cents.

September, 1932 (Vol. 9, No. 3)

RP471. A new determination of the atomic weight of osmium. Raleigh Gilchrist. Price 5 cents.
RP472. "Moisture expansion" of ceramic whiteware. R. F. Geller and A. S. Creamer. Price 5 cents.
RP473. Infra-red arc spectra photographed with xenocyanine. W. F. Meggers and C. C. Kiess. Price 5 cents.
RP474. Tensile properties of cast nickel-chromium-iron alloys and of some alloy steels at elevated temperatures. William Kahlbaum and Louis Jordan. Price 5 cents.
RP475. The comparison of high voltage X-ray generators. Lauriston S. Taylor and K. L. Tucker. Price 5 cents.
RP476. The structure of the chromic acid plating bath: The theory of chromium deposition. Charles Kasper. Price 5 cents.
RP477. Physical properties and weathering characteristics of slate. D. W. Kessler and W. H. Sligh. Price 5 cents.
RP478. Radiation from cæsium and other metals bombarded by slow electrons. C. Boeckner. Price 5 cents.
RP479. A simplified precision formula for the inductance of a helix with corrections for the lead-in wires. Chester Snow. Price 5 cents.
RP480. Register studies in offset lithography. C. G. Weber and R. M. Cobb. Price 5 cents.
RP481. Creep at elevated temperatures in chromium-vanadium steels containing tungsten or molybdenum. William Kahlbaum and Louis Jordan. Price 5 cents.

October, 1932 (Vol. 9, No. 4)

RP482. The synthesis, purification, and certain physical constants of the normal hydrocarbons from pentane to dodecane, of *n*-amyl bromide and of *n*-nonyl bromide. B. J. Mair. Price 5 cents.
RP483. A study of some ceramic bodies of low absorption maturing at temperatures below 1,000° C. R. F. Geller and D. N. Evans. Price 5 cents.
RP484. The determination of magnesia in phosphate rock. James I. Hoffman. Price 5 cents.
RP485. Collisions of the first and second kind in the positive column of cæsium discharge. F. L. Mohler. Price 5 cents.
RP486. The areas and tensile properties of deformed concrete-reinforcement bars. A. H. Stang, L. R. Sweetman, and C. Gough. Price 5 cents.
RP487. A calorimetric method for determining the intrinsic energy of a gas as a function of the pressure. Edward W. Washburn. Price 5 cents.
RP488. The photographic emulsion: Variables in sensitization by dyes. Burt H. Carroll and Donald Hubbard. Price 5 cents.
RP489. A method for the separation of rhodium from iridium and the gravimetric determination of these metals. Raleigh Gilchrist. Price 5 cents.

Research papers, where price is given, are already available, and others will be available in the near future as separates for purchase from the Superintendent of Documents, United States Government Printing Office, Washington, D. C.

U. S. DEPARTMENT OF COMMERCE
ROY D. CHAPIN, Secretary
BUREAU OF STANDARDS
LYMAN J. BRIGGS, Acting Director

BUREAU OF STANDARDS JOURNAL OF RESEARCH

February, 1933
Vol. 10, No. 2

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON: 1933

For sale by the Superintendent of Documents, Washington, D. C. - - - Price 25 cents; $2.50 per year on subscription

For a partial list of previous research papers appearing in BUREAU OF STANDARDS JOURNAL OF RESEARCH see pages 2 and 3 of the cover

THE ELIMINATION OF BACKGROUND "NOISE" IN SENSITIVE PULSE AMPLIFIERS

By L. F. Curtiss

ABSTRACT

A study has been made of the problem of reducing the background "noise" in a high-gain resistance-capacity coupled pulse amplifier used for registering ionization of individual ionizing particles. It has been found that, even after due care has been taken to reduce disturbances in the first two stages, a great improvement can be effected by suitable modification of the final or output stage. This consists in using several output tubes, preferably pentodes, in parallel, and selecting an operating point on the characteristic curve such that small fluctuations in the voltage applied to the control grids produce practically no change in the plate current and yet all pulses which exceed these fluctuations in the desired direction are reproduced in the plate current. Although this arrangement involves some distortion of very small pulses, the gain in the legibility of the oscillograph record is sufficient to compensate for this slight disadvantage. The results obtainable under various conditions are illustrated by reproductions of oscillograph records.

CONTENTS

	Page
I. Introduction	151
II. Modification of output stage	152
III. Advantages of method	153
IV. Acknowledgments	154

I. INTRODUCTION

Vacuum tube amplifiers, capable of registering directly the current pulses produced in shallow ionization chambers when separate α or H particles pass through, are limited in degree of amplification by background fluctuations or "noise." This noise becomes more troublesome as the amplification is increased until a state is reached where it may even mask entirely the current pulses from the ionization chamber. It may arise from a variety of causes, such as absorption of charge in the insulators of the ionization chamber, variations in electron emission from filaments of vacuum tubes, Johnson effect in resistors, and mechanical vibration of parts of the amplifier. All these causes can be dealt with more or less effectively by proper attention to the factors involved. However, noise is usually present to an annoying degree in all amplifiers which are capable of registering the ionization pulses of swift H particles arising from atomic disintegration.

In dealing with this problem it has been customary to give particular attention to the first stages of the amplifier, since any disturbance generated here is amplified in later stages. While investigating the possibilities of reducing the effects of this noise, the writer found that a considerable improvement could be effected by a simple modification of the output stage. This additional control is practicable because of the peculiar nature of a pulse amplifier used to amplify a unidirectional pulse.

II. MODIFICATION OF OUTPUT STAGE

The change from usual practice which has been found effective consists in using two or more tubes in parallel in the output stage and selecting an operating point on the grid voltage-plate current characteristic such that small fluctuations are suppressed without seriously distorting the pulse. This is only possible when the usual precautions have been taken to have the amplifier reasonably free from noise. It is necessary that the smallest pulses to be recorded be definitely larger than the background fluctuations. Under these conditions it is possible to suppress the noise almost entirely without greatly reducing the amplitude of pulses which may be only twice as large as the noise fluctuations. This makes the oscillograph record much easier to read and interpret since even the small pulses stand out sharply. Under the usual conditions it is often difficult to pick these out with certainty from the background disturbance.

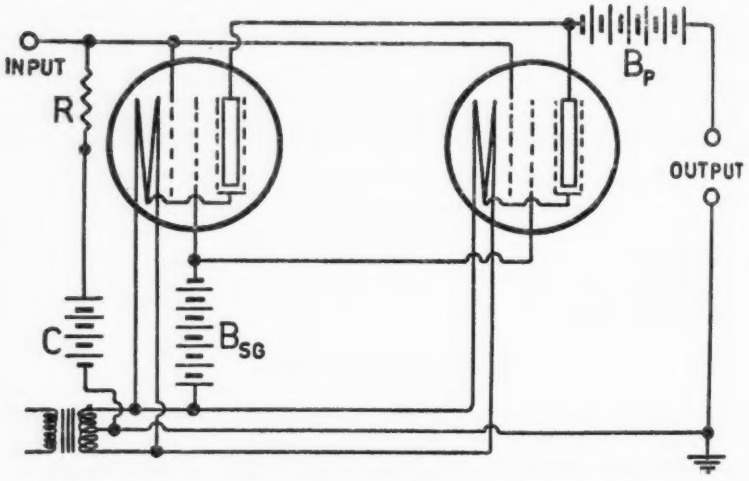


FIGURE 1.—*Diagram of connections showing two pentodes in parallel*
R=0.5 megohm, C=22½ volts, B_{SG}=175 volts, B_P=250 volts

In this method of suppressing noise it is essential that the output stage should receive a positive impulse from the preceding stage when a pulse comes through. It is also desirable to use two or more pentodes in parallel in the output stage as shown in Figure 1. It is then possible to select a bias of such value that the tubes are normally at a point on their characteristic where the curve is practically horizontal but such that a slight shift of the grid potential in the positive direction will cause an increase in the plate current. If the noise fluctuations are not sufficient to raise the potential of the grid above this critical potential, they will not appear in the plate current.

A clearer understanding of how this is possible may be obtained by reference to Figure 2, which is an actual grid voltage-plate current characteristic for two pentodes in parallel. The part of the characteristic below a grid potential of about −15 volts is nearly horizontal but above this potential it rises rapidly to the linear part of the curve. It can be seen at once that, if the incoming signals applied to the grid

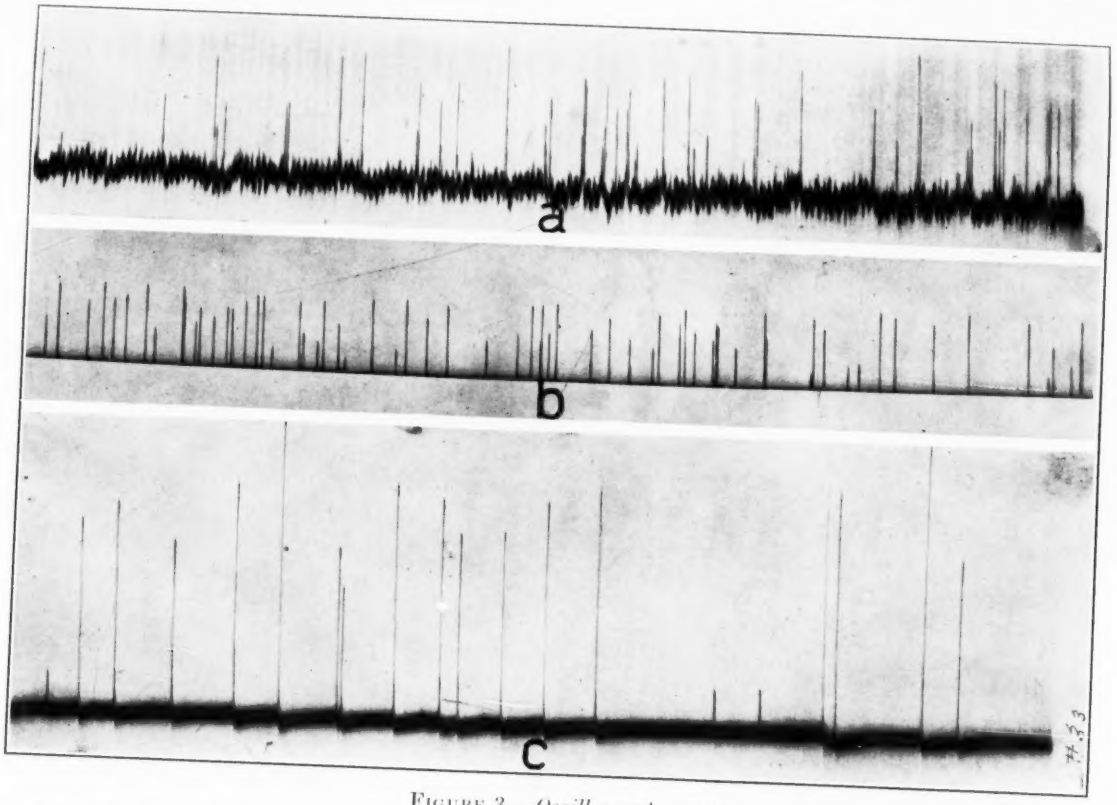


FIGURE 3.—*Oscillograph records*

a, Record obtained with usual output stage of one pentode biased to a steady plate current of 20 milliamperes; b, record with modified output stage; and c, record with modified output stage and a stepdown output transformer.

of these tubes are made up of a pulse S and a background noise represented by B in order of magnitude (this represents about the ratio of the pulse produced by very swift α-particles to the noise in a sensitive amplifier) and the steady grid bias is chosen at about -17 volts, the background will fail to produce any noticeable effect on the plate current, while the signal will be reproduced with only slight distortion. Even for the case of a disintegration proton, which would give a pulse approximately one-eighth of S, the distortion is not sufficient to render its detection difficult. When more accurate measurement is required, the correction for this distortion can be determined experimentally for a given amplifier.

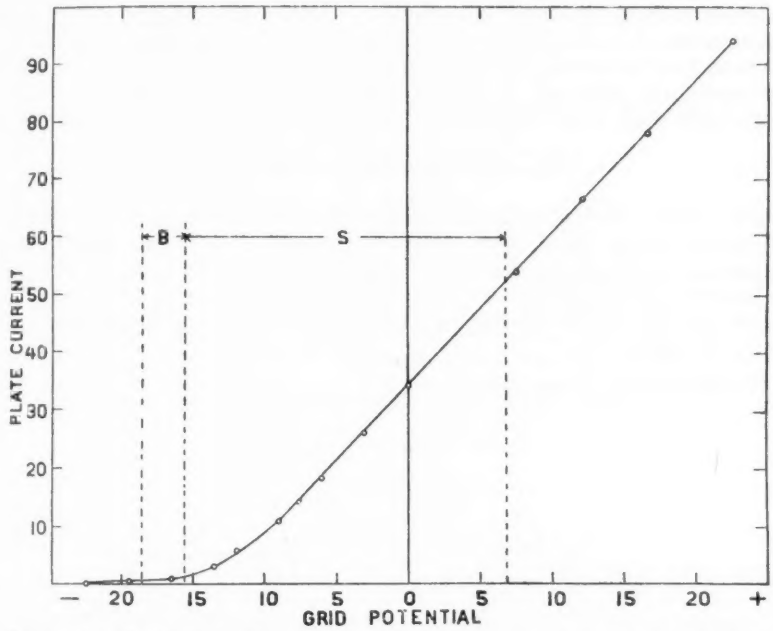


FIGURE 2.—*Grid voltage-plate current characteristic for two pentodes in parallel*

III. ADVANTAGES OF METHOD

The advantages of this modification of the output stage can be shown most readily by a comparison of oscillograph records obtained under various conditions. In Figure 3 a record is shown at (a), obtained with a single pentode biased to give a steady plate current of about 20 milliamperes. It is connected in the output stage of a 5-stage amplifier described elsewhere.[1] In this record the pulses due to α-particles are readily distinguishable, but it is almost impossible to identify and separate those due to protons from the background. At (b) is shown a record obtained with the same adjustment of the amplifier but using the modified output stage described above. This record shows that the noise has been suppressed entirely, resulting in a considerable gain in legibility.

[1] B. S. Jour. Research, vol. 9 (RP461), p. 115, 1932.

Records (*a*) and (*b*) were obtained by connecting a low-resistance bifilar oscillograph directly into the plate circuit of the output stage. This arrangement is very inefficient, since the optimum load resistance of a pentode is about 7,000 ohms. The situation calls for the use of an output transformer, but such a transformer would be of no use when supplied with an input current such as is shown at (*a*). However, using the modified arrangement and an output transformer of relatively low ratio (4:1), the record shown at (*c*) was obtained. In this, the peaks for all slow α-particles go entirely out of the picture. Those whose tops are visible represent either swift α-particles, extending more than halfway across the record, or protons. The pulses produced by the protons are roughtly one-fifth the amplitude of those caused by swift α-particles. Although a slight amount of disturbance due to noise can be seen in the background, it has been reduced to a point where all genuine pulses stand out clearly. Where circumstances demand, a transformer ratio of 16:1 could be used to advantage with a corresponding increase in the size of the deflections

IV. ACKNOWLEDGMENTS

The writer wishes to acknowledge the assistance of B. W. Brown for considerable help with these experiments and in making the numerous oscillograph records required. The polonium source used in testing the amplifier was obtained from material furnished the writer by Dr. C. F. Burnham and Dr. F. West, of the Howard A. Kelly Hospital.

WASHINGTON, December 1, 1932.

THE PRESSURE OF SATURATED WATER VAPOR IN THE RANGE 100° TO 374° C.

By N. S. Osborne, H. F. Stimson, E. F. Fiock, and D. C. Ginnings

ABSTRACT

The method and apparatus employed, and the measurements made in this determination of the vapor pressure of water are described, and the results obtained are given and formulated.

The method used was the "static method" in which the pressure is determined at the stationary boundary between the liquid and the vapor in equilibrium at a contant temperature in a closed container.

The container for the water sample was a calorimeter specially built for high pressure work. Pressures were measured by a precision piston gauge which balances the pressure by the gravitational force on a piston loaded with weights. Temperatures were measured by platinum resistance thermometers supplemented by thermoelements.

A total of 394 measurements were made at 38 temperatures so distributed as to facilitate formulation of the pressure-temperature relation.

The formulation was made by using an empirical equation which was fitted to the results in two temperature ranges. Values of pressure and its derivative with respect to temperature are tabulated from this formulation in standard atmospheres, centibars, and kg/cm² at each degree centigrade, and in pounds per square inch at each degree Fahrenheit. This provides a mutually consistent group of vapor pressure tables in convenient form for practical working tables of fundamental steam data.

It is estimated that the results are reliable to 3 parts in 10,000.

CONTENTS

	Page
I. Introduction	155
II. Method and apparatus	156
1. General description	156
2. Calorimeter shell	158
3. Calorimeter heater	158
4. Heater diffuser	159
5. Envelope	159
6. Connections to the calorimeter shell	160
7. Pressure connections and auxiliary indicators	160
8. Pressure gauge	162
9. Thermometric installation	163
(*a*) Reference block	163
(*b*) Thermoelements	163
(*c*) Resistance thermometers	165
III. Experimental procedure	166
IV. Results of measurements	168
V. Formulation of results	176
VI. Estimation of accuracy	188
VII. Acknowledgment	188

I. INTRODUCTION

The relation between the temperature and the pressure of saturated water vapor is of prime importance in establishing the thermodynamic behavior of steam. This relation, commonly called the vapor pressure relation, is a characteristic property which can be observed

directly. Moreover, its derivative is an essential factor in correlating other important thermodynamic properties. It is evident that adequate knowledge of this property is indispensable to the success of any systematic effort to determine and formulate the thermal properties of steam.

The vapor pressure measurements to be described here were made as a coordinate part of the larger and more formidable project of calorimetric measurement of the enthalpy (heat content) of saturated water and steam. Since pressure and temperature of saturated vapor are definitely related, measurements of other thermal properties may be referred to either temperature or pressure as an independent variable, depending on which is the more expedient. This characteristic was utilized in planning a new high pressure calorimetric [1] apparatus for surveying the bahavior of saturated steam. As a refinement in technique, provision was made for observing both the temperature and the pressure of a water sample in the calorimeter. The arrangements for control and measurement of temperature, and for transmission of pressure to the measuring gage, were perfected to a degree which permits the rapid and reliable measurement of saturation pressure in the range 100° to 374° C.

Measurements within this range have already been made in several laboratories in accordance with definitely specified, recognized standards, permitting reduction of the results to a common basis. The results of these independent determinations, differing considerably in method and technique, have been regarded as in virtual agreement for technical purposes. Nevertheless, close scrutiny disclosed discrepancies which seemed unnecessarily large, particularly in the derivative on which reliance must be placed for making thermodynamic correlations of other experimental data.

The equipment available in this laboratory provided a favorable opportunity for making vapor pressure measurements. These were undertaken prior to the calorimetric measurements with the object of further verifying the numerical values of this property.

To provide for trustworthy correlation of thermodynamic properties, it is necessary not only that the observations of the corresponding pressures and temperatures be adequate in number, distribution, and precision, but also that a formulation be used which yields reliable values of the derivative. This latter requirement has been met by the successful application of a type of empirical equation which conforms with remarkable fidelity to the observed behavior of saturated steam.

II. METHOD AND APPARATUS

1. GENERAL DESCRIPTION

In the calorimetric equipment used in making the vapor pressure measurements, provision is made for observing temperature, pressure, mass of water sample, and the energy added. The arrangements provided for controlling the state of the fluid in the calorimetric experiments are also especially appropriate for the determination of vapor pressure. In this report, which concerns only the latter, the

[1] Mechanical engineering, vol. 54, No. 2, p. 118, 1932.

description is intended to record those features which are essential to the vapor pressure measurements.

A schematic diagram of the vapor pressure measuring equipment is shown in Figure 1. The metal calorimeter shell contains, besides the water sample, an electric heater and a system of radial silver plates for diffusing heat. This shell is suspended within a thermally controlled inclosure or envelope which shields it against heat exchange with the surroundings.

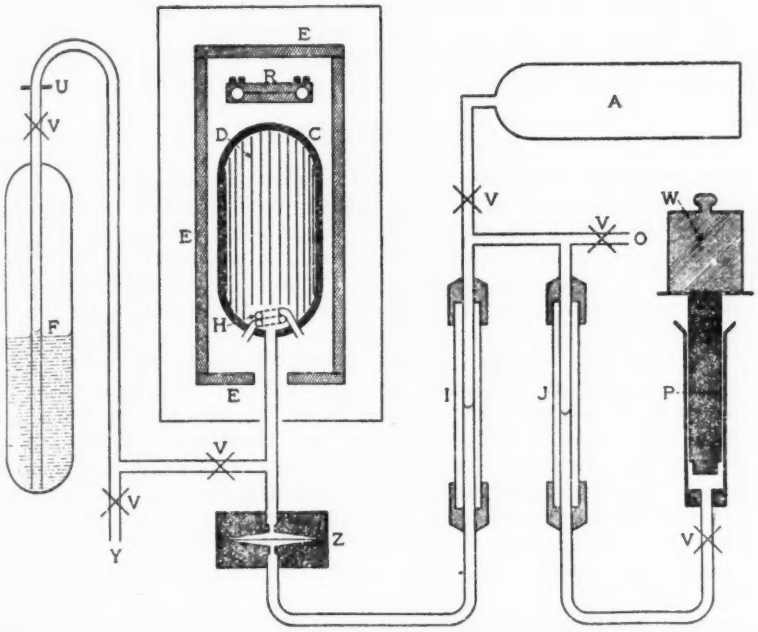


FIGURE 1.—*Schematic diagram of the vapor pressure measuring equipment*

A, high pressure air.
C, calorimeter shell (special steel).
D, heat diffusing system (silver).
E, envelope (silver).
F, water container (silver).
H, electric heater.
I, water indicator (glass capillary).
J, oil indicator (glass capillary).
O, air vent.
P, piston.
R, reference block (silver).
U, union.
V, valves.
W, weights.
Y, vacuum connection.
Z, pressure transmission cell.

The pressure in the calorimeter is transmitted directly through a tube from the bottom of the calorimeter shell to a cell with a thin elastic metal diaphragm which readily transmits pressure, yet prevents escape of the water sample. The pressure in the calorimeter is thus transmitted through this sensitive diaphragm to a column of water, and through this column to a balancing artificial atmosphere of air. The meniscus between the water and air is visible in a glass capillary, and serves to indicate balance between the air pressure and the pressure in the calorimeter. The pressure of the artificial atmosphere which is subject to very delicate manual control, is transmitted to the measuring piston gage through an oil column. The air-oil meniscus is visible in another glass capillary and is used as an indicator to show when the piston is properly loaded.

The temperature of the water sample, which is observed after the load on the piston has been properly adjusted, is obtained by the combined use of platinum resistance thermometers and thermoelements. Resistance thermometers located in a reference block of thick silver, yield the temperature of the block according to the international temperature scale. The thermoelements, with principal junctions distributed on the shell and reference junctions located on the reference block, indicate the small differences which exist between the calorimeter and the reference temperature. The thermoelements can be used in series to indicate average temperatures, or individually to indicate local temperatures. A diagrammatic scale drawing of the assembled apparatus is shown in Figure 2. The principal parts will be described in detail forthwith.

2. CALORIMETER SHELL

The calorimeter shell shown at *C* in Figure 2 provides a receptacle for the sample of water so that its thermal behavior may be observed. It has the shape of a cylinder with hemispherical ends and, as assembled with the various accessory parts in place, will hold approximately 320 cm^3. The material is a special alloy steel containing about 19 per cent chromium, 7.5 per cent nickel, 4.5 per cent tungsten, 1.3 per cent silicon, 0.5 per cent manganese, and 0.46 per cent carbon. This material was chosen because of its resistance to creep and to attack by water at temperatures up to 400° C. The shell was machined from a solid bar and was made in two similar parts held together on a thin silver gasket by the tension developed in the right and left threaded band which is screwed on with powerful wrenches engaging machined lugs. This annular joint was formed by machining one member to a plane surface and the other to a blunt angled edge, giving a contact with the silver gasket of about a half millimeter width. All parts were accurately machined and the surfaces well polished.

The shell, having a thickness of 0.125 inch (3.2 mm), was designed to stand steam pressures up to the critical without permanent deformation. Actually in hydraulic proof tests, it showed no permanent stretch for an internal pressure of 4,500 lbs./$inch^2$. After carrying a charge of water at 350° C., the inner surface showed on examination no sign of attack by the water other than the formation of a very thin film of light-straw color similar to that formed on the outside where in contact with air.

3. CALORIMETER HEATER

The electric heater in the calorimeter shell, shown at *H*1 (fig. 2) is an insulated resistor encased in a metal tubular coil sealed hermetically to the shell. It consists of about 10 ohms of calido wire, 0.2 mm in diameter, with gold leads. This resistor was wound in helical form, 0.6 mm outside diameter, and embedded in magnesia for insulation. It was sheathed in a platinum tube drawn down tightly on the magnesia to an outside diameter of about 2 mm. This sheathed resistor was then bent into the form of a helical coil 12 mm outside diameter, the resistor occupying about two turns. Each projecting end of this heater was put through a threaded plug of silver-palladium alloy and sealed by soldering with gold. To

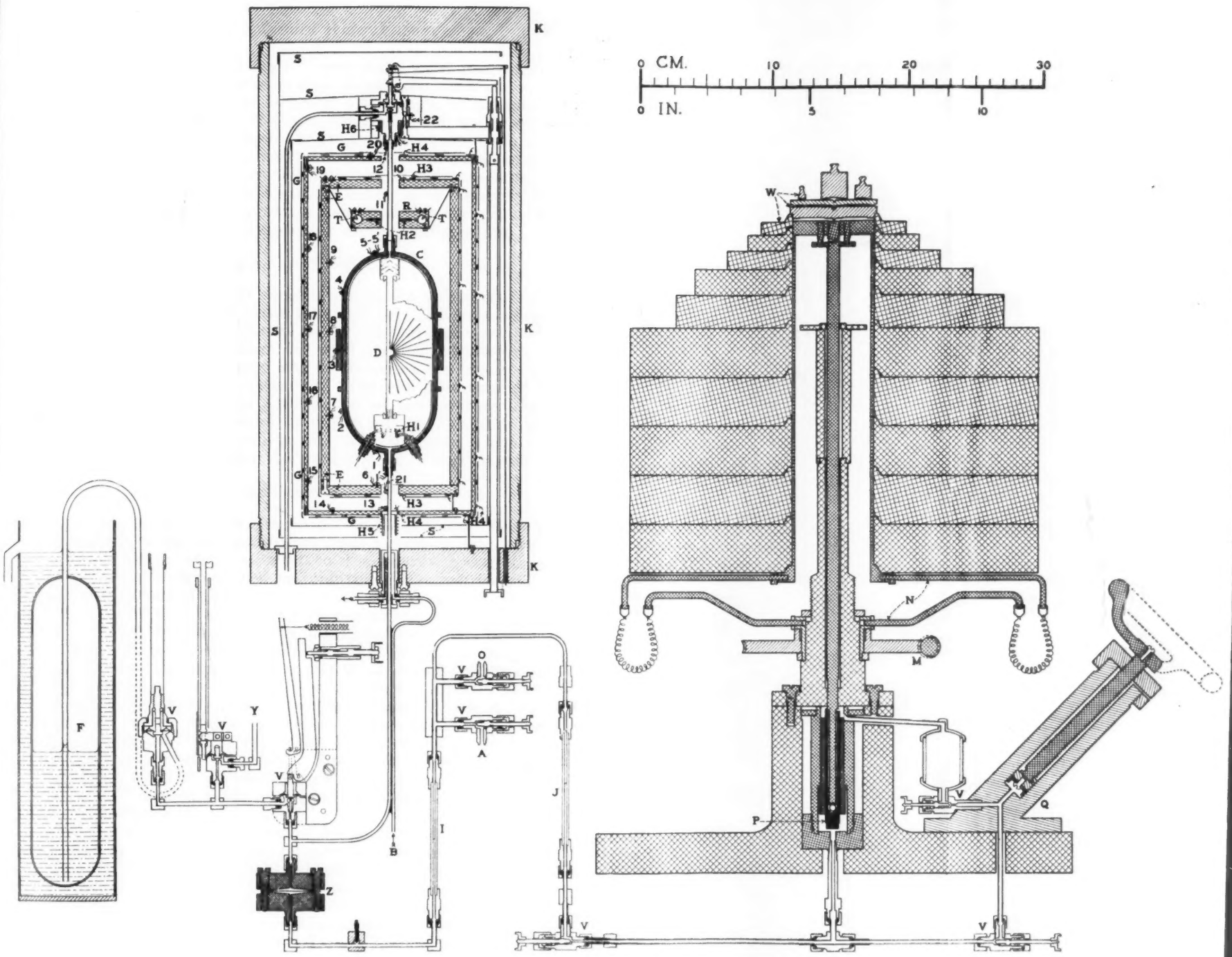


FIGURE 2.—*Sectional scale drawing of vapor pressure measuring equipment*

(NOTE.—This is not a true section but shows sections of important parts projected on a plane.)

A, high pressure air inlet.
B, cooling water.
C, calorimeter shell (special steel).
D, heat diffusing system (silver).
E, envelope (silver).
F, water container (silver).
G, guard (silver).
H_1, *H_2*, etc., electric heaters.
I, water indicator (glass capillary).
J, oil indicator (glass capillary).
K, casing (brass).
M, gear drive.
N, rotating arms.
O, air vent.
P, piston.
Q, oil pump.
R, reference block (silver).
S, shields (aluminum).
T, platinum resistance thermometers.
V, valves.
W, weights.
Y, vacuum connection.
Z, pressure transmission cell.
1, *2*, etc., principal junctions of thermoelements.

152894—33. (Face p. 168.)

complete the seal, the shoulders of these plugs were drawn tightly on thin silver gaskets by threaded nuts outside the shell.

The design of this heater was chosen with regard to influence on the calorimetric performance of the instrument. The heater surface has been made small with three objects in view, namely, to avoid unnecessary heat capacity, to permit operation with small amounts of liquid, and to avoid excessive accumulation of energy as superheat in the liquid. The characteristics of the heater have relatively little to do with the technique of pressure measurements since it is used only for bringing the water sample to a desired temperature.

4. HEAT DIFFUSER

For promoting temperature equalization in the calorimeter shell, a system of heat-conducting plates is provided. This heat-diffusing system consists of 30 flat plates of silver 0.5 mm thick, shaped to conform to the vertical profile of the shell and held radially in two slotted hubs so as to penetrate and interconnect the space within the shell with a good heat conductor. The chief function of this arrangement is to hasten the equalization of temperature after a period of change. This feature is important in both the calorimetric and the pressure measurements, and to some extent compensates for the lack of positive circulation by mechanical means.

5. ENVELOPE

The principal purpose of the envelope which surrounds the calorimeter shell is to provide protection from fortuitous exchanges of heat. This feature, which is vital to the energy accounting in calorimetry, contributes to the suitability of the instrument for pressure measurements by favoring the attainment of thermal equilibrium of the water sample and its container.

This protecting envelope is a double-walled inclosure formed of two coaxial cylindrical silver shells with flat ends, the inner one 6.3 mm thick and the outer one 3.2 mm thick, which will be designated as "envelope" and "guard" respectively. Electric heating elements are distributed over the outer surfaces of these shells. Subdivision of these heaters provides for meeting various local thermal requirements. The heater on the envelope is used only when its temperature is being raised. The guard may also be heated at a controlled rate, or its temperature may be maintained automatically at any desired value by a sensitive thermoregulator using a platinum resistance thermometer.

At a steady temperature the guard heater supplies the heat loss to the outside while the envelope temperature remains fixed. Such conditions are favorable for the establishment and maintenance of temperature equality of the calorimeter and its contents.

In the space outside the guard two thin aluminum shields are placed to impede the loss of heat by radiation and convection. These light shields, 0.05 mm thick, furnish effective thermal insulation and prevent excessive heat loss without introducing any considerable thermal lag. The whole is inclosed in a heavy brass casing which serves not only as a cover but also as protection in case of an explosive failure.

6. CONNECTIONS TO THE CALORIMETER SHELL

The calorimeter shell is held in place by two tubes of silver-palladium alloy. The one at the top bears the weight of the shell and the one at the bottom centers it. Besides furnishing firm, thermally resistant support for the shell, these tubes serve also for the transfer of fluid to or from the calorimeter. The upper tube is intended for a vapor outlet to be used in calorimetric measurements of heat of vaporization and was temporarily closed during the pressure measurements by a disk in the union at the top of the shell. This suspension tube reaches from the body of the vapor valve which is carried on a light but firm support from the guard shell.

The lower tube is used as a connection to transfer liquid to or from the calorimeter, and also to transmit pressure from within to the auxiliary measuring equipment outside. A cylindrical brass cell for cooling water surrounds this tube where it passes through the outer brass casing. Where the tube passes through the outer silver guard shell it bears an electric heater mounted on a silver support attached to the tube. There is a free length of about 2.6 cm between this heater and the union at the shell. The purpose of the heater is to control the thermal gradient in this section of the tube as indicated by thermoelements installed for that purpose. Similarly, the gradients on the upper tube are controlled by a heater on the vapor valve body.

The lower tube is always filled with liquid while observing saturation behavior in the calorimeter. From a union just below the cooling cell at the bottom, connection is made through a copper-nickel tube to the liquid valve and the pressure transmission cell. Beyond the liquid valve the line extends to a union by which the water receiver with its valve is connected. A side connection leads through a valve to a vacuum pump to permit evacuation of the calorimeter and its connecting lines.

7. PRESSURE CONNECTIONS AND AUXILIARY INDICATORS

Pressure is transmitted from the free surface of the liquid in the calorimeter through a continuous column of liquid water to the elastic diaphragm of the pressure transmission cell to be described forthwith. The purpose of this cell is to allow the pressure in the calorimeter system to be communicated to the pressure measuring gage, while at the same time interposing a barrier to the escape of water from the system through the gage line. A limited amount of inward and outward movement is allowed the water column by the necessary flexibility of the transmitting device, but this movement is restricted to the small volume displacement of 0.04 cm^3 required for observation. In this transmitting cell, a circular diaphragm of thin silver about 3 cm in diameter is held under slight tension between the two parts of the cell which clamp the diaphragm tightly near the edge. Small pressure changes suffice to move the diaphragm back and forth across the space between the two parts. The inner cell walls are shaped to conform approximately to the figure of the distended diaphragm. The delicate diaphragm must encounter support from the cell walls to avoid deformation beyond its elastic limit when the pressures are far out of balance.

The cell is made of two disks of stainless steel, each about 5 cm in diameter and about 1.4 cm thick, provided with 12 screws to draw them tightly together on the silver diaphragm. The two parts have nipples with unions for making connections with the lines as shown. The apertures to the inner cell are made only 0.035 cm in diameter to avoid too large an unsupported area of the thin silver diaphragm. This diaphragm is a vital part of the device, and its characteristics determine the limit of sensitivity of the transmitting cell. It is of rolled sheet silver about 0.06 mm thick. The diaphragm and cell were put together at a temperature of about 150° C. in order to produce sufficient tension, when cooled, to flatten out the slight unevenness of the sheet which otherwise would interfere with the freedom of motion between the cell walls. This procedure left enough flexibility to give a satisfactory sensitivity to pressure change.

On the measuring or gage side of the diaphragm a continuous column of liquid water extends and transmits pressure to air at the meniscus boundary in a glass capillary indicator. The volume of this water column is small. The meniscus is a reliable indicator of the position of the diaphragm and is used as a null device to tell when the pressures on the two sides are balanced to bring the diaphragm to a chosen zero position near the neutral. The air column extends to the end of an oil column in a second glass capillary indicator, whence the pressure is transmitted through the oil directly to the piston of the measuring gage. Sensitive needle valves permit fine adjustment of the pressure in the air line to balance the pressure in the calorimeter. When these pressures are balanced and the piston gage is also balanced by weights, the vapor pressure in the calorimeter may be found from the pressure measured at the piston by taking into account the fluid columns between the piston and the free surface in the calorimeter and whatever pressure difference the diaphragm may support.

The fluid columns to be accounted for are the oil, air, and water columns. The oil-column correction is constant and is easily measured. The air-column correction depends on the pressure and is almost negligible. The correction for the water column is somewhat more complicated due to the variation of the position of each end. The position of the meniscus in the glass capillary is directly observed and easily corrected for in each measurement. From a reference point on this capillary to a point near the calorimeter there is a constant pressure correction which is computed from the difference in height. From this latter point to the free surface the pressure correction varies both with the filling in the calorimeter and with its temperature, and was computed for the conditions of each measurement.

The correction for pressure difference supported by the diaphragm is small, but arises because the chosen zero position is not necessarily the neutral or unstrained position. It was determined by making a vapor pressure measurement near 100° C. with the air column open to the atmosphere instead of being connected to the piston gage. Since the vapor pressure of water is one standard atmosphere at 100° C. by definition of the international temperature scale, and its temperature variation there is well known, the difference between the computed pressure at the open end and the observed barometric pressure gives the desired diaphragm zero correction. This correction was determined occasionally during the progress of measurement.

This method of calibration connects the scale of pressure with the standard unit at the one atmosphere fixed point and in effect includes that point in the range of the observations.

A preliminary calibration of the assembled diaphragm with its capillary indicator was made at atmospheric pressure to determine its sensitivity to pressure differences. This showed the diaphragm displacement to be nearly proportional to the pressure difference over a considerable portion of the middle range. Within this linear range a pressure difference of 0.001 atmosphere was found to correspond to about 0.6 mm on the capillary indicator. This sensitivity calibration is merely an index of the limit of precision to be expected when the diaphragm is set to a chosen zero position and does not enter into the reduction of the observations.

8. PRESSURE GAGE

The pressure-measuring gage used in these determinations was one of a group of piston gages whose construction and calibration have been described previously.[2] These gages were designed and built at this bureau to meet a need for precision pressure-measuring instruments in determining thermodynamic properties of fluids. They have been studied with great care to determine their reliability as standard instruments.

This type of gage employs a loaded rotating piston which is supported in a vertically mounted, closely fitting cylinder by oil under the pressure to be measured. A balancing load of weights on the piston is borne axially above it on a carrier which engages the piston. A horizontal couple applied to the carrier by motor-driven arms produces a slow continuous rotation which is transmitted through it to the piston. Thus the entire load consisting of piston, carrier, and weights is rotated without introducing any appreciable vertical component of driving force. The rotation of the piston maintains a lubricating film of oil between it and the closely fitting cylinder. This provides greater freedom for vertical motion of the loaded piston in case of unbalance, by preventing direct contact between the piston and cylinder.

The gage chosen for the present work and shown in Figure 2 has a piston area of about 1 cm^2. It was designed for the range from about 3 to 100 atmospheres pressure. As it was desired to cover the range of steam pressures from 1 atmosphere to 218 atmospheres, it was necessary to make some modification to provide for this extension of the range. This was done by substituting for the original weight carrier two special ones, the first very light to permit a small load on the piston, and the second a larger carrier to accommodate the extra weights for the high pressures. This gage is provided with a set of weights in units ranging from 20 to 0.1 kg, specially built to stack on the carrier with proper stability. Standard laboratory weights were used for the range 100 to 1 g. The weights were calibrated at the time of their use in these measurements, and corrections were applied where significant.

The effective piston area had been determined in 1928 by a series of calibrations using a multiple-column mercury manometer as the fundamental standard. Direct comparisons with this standard

[2] Meyers and Jessup, B. S. Jour. Research, vol. 6, (p. 324), June, 1931.

manometer were made at a pressure of 15 atmospheres. In addition to these, comparisons were made at pressures up to 75 atmospheres, using another gage to step up from the 15-atmosphere limit of the manometer to the higher pressures. These calibrations all gave a value of 0.9961 cm^2 at 20° C. for the effective piston area at that time.

During the course of the present pressure measurements a comparison was made with two other similar standard piston gages, and with the vapor pressure of a standard sample of carbon dioxide as a precaution against any significant change in the effective piston area which might have occurred since its 1928 calibration. The results of these comparisons gave the same value of 0.9961 cm^2.

9. THERMOMETRIC INSTALLATION

The thermometric installation used in the control and measurement of the temperature of the water sample includes platinum resistance thermometers and thermoelements. Thermoelements alone suffice for the survey of temperature distribution. For determining the actual temperature of the water sample, certain of the thermoelements are used to supplement the indications of platinum resistance thermometers.

(a) REFERENCE BLOCK

A silver reference block located in the space above the calorimeter shell serves as an isothermal union between the resistance thermometers and the reference junctions of the thermoelements. Thus the thermometers measure the temperature of the reference junctions, while the thermoelements indicate the small additional differences between this reference temperature and those of chosen points where the principal junctions are located.

The reference block is made of two similar rectangular pieces of pure silver, each 5.6 by 3.8 by 0.63 cm, held together flatwise by screws. It is suspended horizontally from the top of the envelope by four slender straps of stainless steel. A pair of electric heaters and two resistance thermometers fit in receptacles machined across the horizontal midsection. A hole 12.7 mm in diameter in the vertical axis accommodates the small tube which suspends the calorimeter shell. This well-conducting block of silver is designed to keep the reference junctions at the same temperature as the resistance thermometers.

(b) THERMOELEMENTS

The temperature-measuring system includes thermoelements with 38 principal junctions. These thermoelements are connected in groups to economize leads and to permit combinations for surveying temperature distribution, for indicating average temperature differences of surfaces, and for determining the temperature of the water sample. These combinations are completed at the option of the observer by the use of specially built distributing switches with all-copper circuits.

The thermoelements which are used to indicate the temperature of the water are a group of five with principal junctions located on the calorimeter shell at points selected as representative. These chosen points lie in one vertical element of the shell. The five junctions, designated as 1, 2, 3, 4, and 5, are spaced as shown in Figure 2. The indications of these five junctions may be observed individually, giving the temperature difference between any zone and the reference

block, or all five may be observed in series to give a composite of the temperatures of the five zones. The single junctions may also be observed differentially against junction No. 5 at the top of the calorimeter to show directly the vertical distribution of temperature on the shell. The ability to make such a temperature survey enables the observer to follow the approach to equilibrium and make due allowance of time to assure a reliable temperature determination.

Each thermoelement is made of one wire of "chromel P," 0.127 mm in diameter, and two wires of "copel," 0.10 mm in diameter, the latter twisted together. For insulation and support, these wires are threaded through thin strips of mica which are assembled with mica separators and covers into sturdy but light and flexible bundles carrying groups of thermoelements.

Each principal junction of chromel to copel is made by silver soldering the wires to a tiny gold terminal which is used to attach the junction in the desired place. The reference junctions, two to each element, are made similarly by attaching gold terminals to the chromel and copel wires. These gold terminals make electrical connection to gold lead wires and provide for attachment of the reference junctions to the reference block.

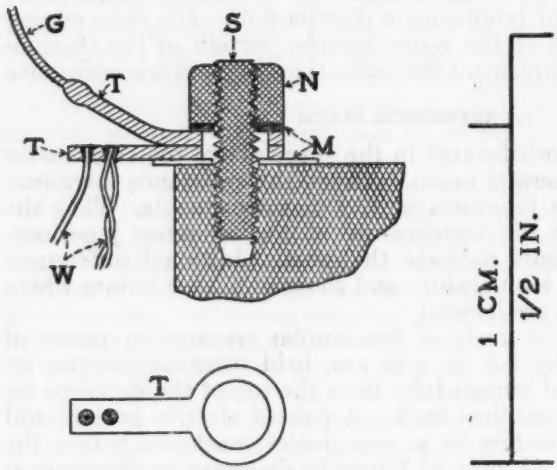


FIGURE 3.—*Details of thermojunction attachment*

G, gold wire. *S*, stud.
M, mica insulation. *T*, gold terminal.
N, nut. *W*, thermoelement wires.

Figure 3 shows how the terminals are installed to secure good thermal union, electrical insulation, and electrical connection where desired. They are held firmly under nuts on threaded studs which are screwed into the metal at the desired places. The terminals are insulated electrically from above and below by mica washers, and from the stud by centering. Additional thermal attachments of the gold lead wires are made in a similar manner at the reference block and at the bottom of the envelope to prevent thermal lead conduction from directly affecting the reference junctions and thus causing erroneous temperature indications.

Gold wires, insulated with mica as described above, are brought out in a bundle from the reference junctions within the heated space to an accessible place at the temperature of the room. Here an isothermal attachment on copper blocks is provided for the junctions between these gold wires and the copper wires which lead across to the observing station.

The electromotive forces of the thermoelements, amounting in nearly all cases to less than 20 mv, are measured on a Wolff poten-

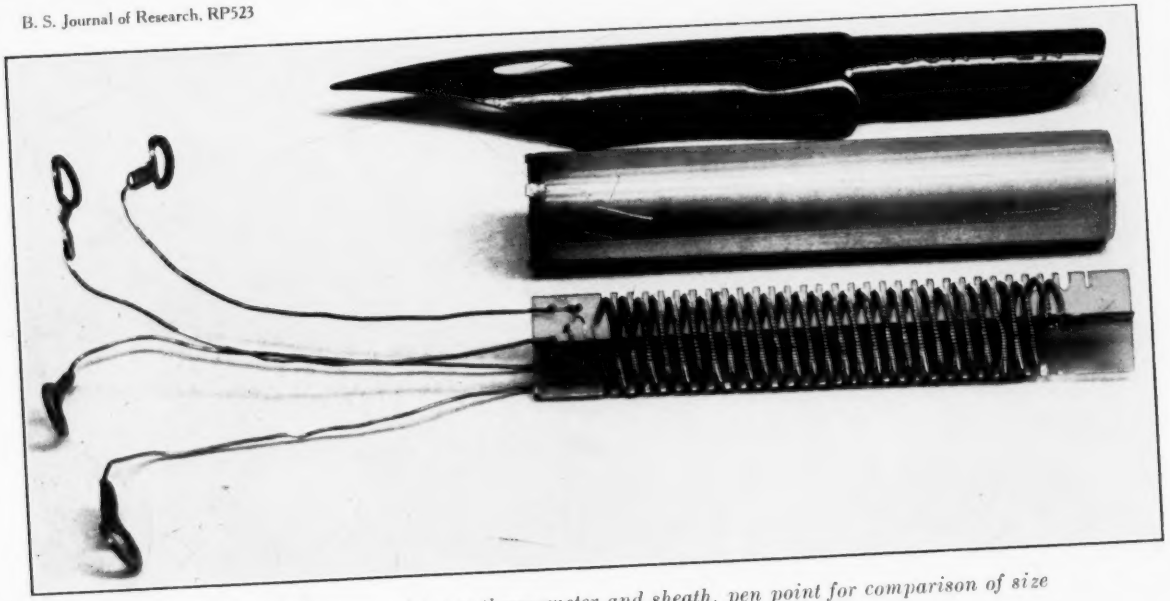


FIGURE 4.—*Platinum resistance thermometer and sheath, pen point for comparison of size*

tiometer designed by F. Wenner. Calibration of this instrument showed its corrections to be negligible. When the temperature of the calorimeter is being observed by means of the five thermoelements in series, a scale deflection of 1 mm corresponds to about 0.001° C.

The five thermoelements which are used in the measurement of water temperature were calibrated in place against a resistance thermometer in the reference block by the following procedure: With the block at nearly the same temperature as the calorimeter, a small emf is indicated on the thermoelements. When the block is heated the thermoelement reference junctions are heated by the same amount as the resistance thermometer. Therefore, the change in thermoelement emf is equivalent to the change in temperature as indicated by the thermometer. Calibrations were made at every temperature where pressure observations were made.

(c) RESISTANCE THERMOMETERS

Two specially constructed platinum resistance thermometers were used as working standards for the temperature measurements. These are of the 4-lead potential-terminal type. They were made small and compact to fit into the receptacles in the reference block. The windings were made of highly refined platinum which showed at 100° C. a resistance as high as 1.392 times that at 0° C. The platinum wire, 0.1 mm in diameter, was first wound in helical form 0.45 mm in diameter, and again wound in a second helical form 4.8 mm in diameter upon a mica cross with the edges notched to carry the winding, yet leave it free from mechanical constraint. Initial strains were relieved by annealing the completed thermometer at 660° C. Each thermometer is mounted in a cylindrical silver case which fits the receptacle in the reference block. Figure 4 shows the construction of one of these thermometers.

This type of thermometer winding has been described by C. H. Meyers [3] and is particularly adapted to use where large size is objectionable. The question as to whether a platinum winding of this compact double-helical type will define the same temperature scale between the fixed points as a winding of the customary strain-free type, has been studied by making a direct comparison between one of the thermometers of this apparatus and one of the earlier standard thermometers of this laboratory. In the interval from 200° to 320° C., the maximum observed difference in indication was at 270° and amounted to 0.013° C., which is not more than that attributable to the uncertainty of reproduction of the scale itself.

The two thermometers used (M–22 and M–26) were selected from a group of eight by consideration of their characteristics and behavior over a period of time. They were calibrated according to the specifications of the international temperature scale, [4] which uses the fixed points of ice, steam, and boiling sulphur as 0, 100, and 444.6°, respectively. The thermometers were calibrated before and during the progress of the pressure measurements and showed no significant changes. The thermometer No. M–22, which was used in all the experiments, had the constants $R_0=27.6637$, $R_{100}=38.5158$, $\delta=1.496$, which were used in the Callendar formula given later for the tem-

[3] B. S. Jour. Research, vol. 9 (RP508), December, 1932.
[4] Burgess, G. K., B. S. Jour. Research, vol. 1 (RP22), p. 635, October, 1928.

perature computation. The thermometer No. M–26, which was used only occasionally to check the other thermometer, had the constants $R_0 = 27.7640$, $R_{100} = 38.6555$, $\delta = 1.496$.

The resistances of the thermometers are measured with a Mueller[5] bridge built by O. Wolff. The bridge coils are immersed in a thermostated oil bath. A separate commutator switch permits the observation of either thermometer. The bridge coils were recalibrated several times during this investigation. A bridge current of 4.5 milliamperes was used both in the calibration and in the measurements of temperature. A galvanometer scale deflection of 1 mm corresponded approximately to 0.0001 ohm, or about 0.001° C. for the thermometers used.

III. EXPERIMENTAL PROCEDURE

The first step in a vapor pressure determination is the introduction of a chosen amount of pure air-free water into the calorimeter. The water used in these measurements was prepared from distilled water by continuous low-pressure distillation in a special apparatus. The air was removed by pumping from the condenser a small fraction of the vapor which carried with it all but a trace of the air dissolved in the original water. This purification was found adequate to avoid any measurable partial pressure of air in the steam. A measured sample of the purified water is transferred without contact with air from the distilling apparatus to a special container, With this container attached to the evacuated calorimeter system, the water is driven into the calorimeter shell by heating the container. Weighing the container before and after this operation checks the amount transferred to the calorimeter. This must be known in order to compute the correction for the height of the liquid at any time.

The calorimeter with its charge of water is next brought to the desired temperature by adding heat electrically. At the same time the envelope, guard, reference block, and connecting tubes are all heated in a similar manner and at about the same rate. Their temperatures are finally adjusted by successive approximations while the calorimeter with its contents approaches the desired uniform stationary temperature. As this chosen temperature is approached, the automatic temperature control of the guard shell is put into operation.

The behavior of the fluid in the calorimeter varies appreciably in the temperature range covered by these experiments. At temperatures below 350° C., thermal gradients produced by heating the fluid, diminish quickly, leaving only small persistent gradients. As the critical region is approached, however, the gradients become larger. The procedure used to hasten favorable conditions for observing pressure at these high temperatures is first to heat the water above the desired temperature and then to cool by lowering the envelope temperature. This produces condensation on the upper calorimeter walls, bathing them with liquid which tends to bring them nearer the effective saturation temperature.

As equilibrium is approached, successive approximations are made to the adjustments necessary for a pressure measurement. The calorimeter pressure is balanced by the air pressure which in turn is balanced by the load on the piston. If the temperature and pressure

[5] Mueller, B. S. Bull., vol. 13, p. 547, October, 1916.

in the calorimeter were stationary and the measuring apparatus adjusted to proper balance, the diaphragm of the pressure cell would be at rest in its zero position, the two capillary indicators stationary, and the loaded rotating piston of the gage neither rising nor falling. This ideal condition of absolute constancy is not necessary to a satisfactory measurement. After close control and adjustment have been obtained, they are held over a period of about two minutes while a series of temperature readings is taken. The definitive value of the load is that at the mid-point of this period. The pressure observation includes the balancing load on the piston, temperature of the piston, barometric pressure, and height of fluid columns in the capillary indicators. The balancing load could always be determined to the nearest gram, and at low pressures it was possible to estimate fractions of a gram. At the higher steam pressures it is unnecessary to determine the load more closely than to 1 g in order to have the precision of the pressure measurement correspond with that of the temperature.

For determining the effective saturation temperature, four successive temperature readings are made at equal time intervals. Each temperature reading consists of simultaneous observations of resistance thermometer and thermoelements. The above method of reading several successive temperatures is desirable for several reasons. First, the 4-lead potential-thermal resistance thermometer requires at least two observations to eliminate the lead resistance from the measurement. Second, increasing the number of readings decreases the accidental error of observation. Third, a regular schedule of readings takes account of slight drift of temperatures. Fourth, the schedule permits the observation of local temperatures during the measurement.

The best selection of thermoelements to determine the temperature of the free surface of the water depends on the temperature distribution and the location of the liquid level in the calorimeter. In the range of temperature below 350° C., the water and calorimeter reach a steady state promptly. Below 200° C. this steady state was a uniform temperature, as indicated by surveys. All five thermoelements were therefore taken to indicate the saturation temperature up to 200° C.

Between 200° and 350° C., after the steady state was reached, the bottom of the shell showed a small persistent depression of temperature and the top a small elevation due to inability to control the surroundings perfectly. In this range the three intermediate thermoelements, Nos. 2, 3, and 4, were used.

Above 350° C. a difference in the behavior of the fluid was observed. The steady state was reached more slowly and thermal gradients were larger over the entire shell. The saturation temperature was estimated from the indication of a single thermo-element located in the vicinity of the liquid level in the calorimeter. If the quantity of water in the calorimeter is checked as previously described, the location of the liquid level is reliably known at temperatures below 370° C. Near the critical region, a comparatively small difference in the water sample determines whether saturated vapor, superheated vapor, or compressed liquid is present. Experiments were therefore made to indicate the state of the water in the calorimeter. These experiments started with the calorimeter supposed to be full of liquid water. After the pressure was observed, a chosen small amount of liquid was with-

drawn and the pressure again observed. This procedure was repeated until the observed pressure, when reduced to a given temperature, showed a constant value indicating existence of the saturation state.

During the progress of the vapor-pressure measurements, two types of experiments were made to prove the absence of an appreciable amount of permanent gas in the calorimeter. In the first type, pressures were measured before and after the withdrawal of liquid, which increased the vapor space in the calorimeter. In the second type, the presence of gas in the calorimeter was tested by a McLeod gage after removal of the liquid. These tests gave no indication of enough gas to affect the vapor-pressure results.

IV. RESULTS OF MEASUREMENTS

The results of the entire series of measurements have been assembled in Table 1, which includes each measured temperature, reduced to degrees of the international temperature scale of 1927 [6] and the corresponding measured pressure reduced to international standard atmospheres.[7] This table also contains the reduction of the observed pressures to values corresponding to even temperatures to permit comparison of the individual determinations and to facilitate the formulation of the entire group of results.

Each measured temperature is computed from the observed data, consisting of four readings of the bridge when balanced with the platinum resistance thermometer in circuit, and the four simultaneous readings of the potentiometer when balanced against the thermoelements, as described above in Section III, Experimental Procedure.

Each measured pressure is computed from the following observed quantities: The load on the piston gage, temperature of gage, position of water meniscus and oil meniscus, amount of water in the calorimeter, and barometer reading, including its temperature.

The auxiliary data used in these reductions include the densities of water and of oil, value of gravity at the Bureau of Standards, the relative elevation of gage and barometer from the gravity bench mark, the results of calibrations of the bridge, resistance thermometers, thermoelements, and the piston gage with its connecting lines and weights.

The mean of the four bridge readings corrected for the bridge calibration gives the resistance of the platinum thermometer (R_θ) at the mean temperature of the series. The temperature, θ, is computed from this resistance by use of the Callendar formula

$$\theta = 100\ (R_\theta - R_0)/(R_{100} - R_0 + 0.01\ \theta(0.01\ \theta - 1)\ \delta$$

The constants R_0, R_{100}, and δ are determined by the calibration previously described.

The mean of the four thermoelement observations is reduced from microvolts to degrees temperature difference by use of the calibration factor determined as previously described. By combining this mean temperature difference between the water and the reference block

[6] Burgess, G. K., B. S. Jour. Research, (RP 22) p. 635, October, 1928.

[7] Standard atmospheric pressure is defined as the pressure due to a column of mercury 760 mm high, having a mass of 13.5951 g/cm³, subject to a gravitational acceleration of 980.665 cm/sec.² and is equal to 1,013,250 dynes/cm², B. S. Jour. Research, October, 1928, p. 637.

and the mean temperature of the block as determined by the thermometer, the temperature of the water, θ_w, is obtained.

The pressure observation, made at the middle of the series of temperature readings, corresponds with the water temperature determined as above. In reducing the pressure observation, the effective weight of the entire load supported by the oil acting on the effective piston area was computed as the sum of the masses of the weights, weight carrier, and the piston, corrected for calibration and air buoyancy. From this total mass the resultant pressure was computed by use of the value of gravity at this laboratory (980.09 cm/sec.^{2}) relative to the standard value of gravity (980.665 cm/sec.^{2}) and the effective piston area, corrected for the effect of thermal expansion. To this component of pressure due to the load was added the observed barometric pressure corrected for temperature, difference in level, and for gravity, thus giving the total pressure at the bottom of the piston. From this pressure at the gage, the pressure at the level of the liquid in the calorimeter was found by applying the following corrections for the intermediate fluid columns: The oil column between the piston and the oil meniscus, the air column between oil and water, the water column between the water meniscus and the water level in the calorimeter, and the correction for the diaphragm position determined by the calibration at atmospheric pressure. The pressure contributed by the liquid water column in the calorimeter was calculated from the mass of water in the calorimeter, the dimensions of the calorimeter and the specific volumes of vapor and liquid water determined by Keyes and Smith.[8]

The total correction for fluid columns in the transmission line did not exceed 0.04 atmosphere and was estimated to 0.0001 atmosphere. The accuracy of this estimation may have limited the precision attainable at the lowest pressures measured. At the higher pressures, it was of less importance in comparison with several other factors.

TABLE 1.—*Observed pressure of saturated water vapor*

Date	Observed quantities		Reduction to even temperature	Vapor pressure at even temperature	Residual
	Temperature θ_w	Pressure P_w		P	$P-P_m$
	°C. (Int.)	Standard atmospheres (Int.)			
July 20, 1932	110.027	1.4146	−0.0013	1.4133	−0.0010
	110.018	1.4152	−.0009	1.4143	.0000
	110.003	1.4149	−.0001	1.4148	+.0005
	110.019	1.4156	−.0009	1.4147	+.0004
July 21, 1932	110.011	1.4148	−.0005	1.4143	.0000
	109.994	1.4138	+.0003	1.4141	−.0002
	110.008	1.4146	−.0004	1.4142	−.0001
	110.027	1.4156	−.0013	1.4143	.0000
Even temperature 110°.	Mean value of pressure at 110 $= P_m = 1.4143$ atm.				
July 20, 1932	119.975	1.9579	+0.0015	1.9594	−0.0004
	119.991	1.9587	+.0006	1.9593	−.0005
	119.981	1.9587	+.0012	1.9599	+.0001
	120.010	1.9608	−.0006	1.9602	+.0004
July 21, 1932	119.982	1.9590	+.0011	1.9601	+.0003
	119.956	1.9564	+.0027	1.9591	−.0007
	120.004	1.9604	−.0003	1.9601	+.0003
	119.988	1.9596	+.0007	1.9603	+.0005
Even temperature 120°.	Mean value of pressure at 120° $= P_m = 1.9598$ atm.				

[8] Mechanical Engineering, vol. 53, No. 2, p. 133, 1931.

TABLE 1.—*Observed pressure of saturated water vapor*—Continued

Date	Observed quantities: Temperature θ_w	Observed quantities: Pressure P_w	Reduction to even temperature	Vapor pressure at even temperature P	Residual $P-P_m$
	°C. (*Int.*)		*Standard atmospheres (Int.)*		
April 2, 1932	129.965	2.6624	+0.0028	2.6652	−0.0008
	129.965	2.6635	+.0028	2.6663	+.0003
	129.965	2.6636	+.0028	2.6664	+.0004
April 5, 1932	130.014	2.6656	−.0011	2.6645	−.0013
April 7, 1932	130.008	2.6644	−.0006	2.6638	−.0020
April 8, 1932	129.996	2.6641	+.0003	2.6644	−.0014
July 2, 1932	129.990	2.6652	+.0007	2.6659	+.0001
	129.971	2.6636	+.0023	2.6659	+.0001
	130.000	2.6660	.0000	2.6660	+.0002
July 7, 1932	130.046	2.6692	−.0037	2.6655	−.0003
July 21, 1932	129.998	2.6665	+.0002	2.6667	+.0009
	129.976	2.6649	+.0019	2.6668	+.0010
	130.003	2.6670	−.0002	2.6668	+.0010
	130.023	2.6686	−.0018	2.6668	+.0010
Even temperature 130°.	Mean value of pressure at 130° = P_m = 2.6658 atm.				
April 2, 1932	140.370	3.6027	−0.0373	3.5654	−0.0007
	140.371	3.6028	−.0374	3.5654	−.0007
	140.371	3.6028	−.0374	3.5654	−.0007
April 5, 1932	140.023	3.5682	−.0023	3.5659	−.0002
April 7, 1932	139.980	3.5614	+.0020	3.5634	−.0027
April 8, 1932	139.983	3.5625	+.0017	3.5642	−.0019
July 2, 1932	139.984	3.5653	+.0016	3.5669	+.0008
	139.968	3.5634	+.0032	3.5666	+.0005
	140.005	3.5675	−.0005	3.5670	+.0009
July 7, 1932	140.004	3.5665	−.0004	3.5661	.0000
July 21, 1932	139.975	3.5654	+.0025	3.5679	+.0018
	139.987	3.5662	+.0012	3.5674	+.0013
	140.021	3.5694	−.0021	3.5673	+.0012
Even temperature 140°.	Mean value of pressure at 140° = P_m = 3.5661 atm.				
March 25, 1932	149.879	4.6802	+0.0152	4.6954	−0.0015
March 28, 1932	149.911	4.6849	+.0112	4.6961	−.0008
March 29, 1932	149.868	4.6789	+.0166	4.6955	−.0014
March 30, 1932	150.032	4.7018	−.0040	4.6978	+.0009
April 1, 1932	149.998	4.6970	+.0002	4.6972	+.0003
April 7, 1932	149.984	4.6922	+.0020	4.6942	−.0027
April 8, 1932	150.004	4.6964	−.0005	4.6959	−.0010
July 7, 1932	150.035	4.7017	−.0044	4.6973	+.0004
July 21, 1932	149.985	4.6971	+.0019	4.6990	+.0021
	150.004	4.6994	−.0005	4.6989	+.0020
	150.025	4.7019	−.0031	4.6988	+.0019
Even temperature 150°.	Mean value of pressure at 150° = P_m = 4.6969 atm.				
April 2, 1932	160.067	6.1101	−0.0104	6.0997	−0.0001
	160.068	6.1102	−.0106	6.0996	−.0002
	160.068	6.1102	−.0106	6.0996	−.0002
April 7, 1932	160.027	6.1028	−.0042	6.0986	−.0012
April 8, 1932	159.990	6.0972	+.0016	6.0988	−.0010
July 2, 1932	160.016	6.1031	−.0025	6.1006	+.0008
	159.999	6.0996	+.0002	6.0998	.0000
	160.022	6.1036	−.0034	6.1002	+.0004
July 7, 1932	160.016	6.1023	−.0025	6.0998	.0000
July 21, 1932	159.965	6.0956	+.0054	6.1010	+.0012
	159.978	6.0950	+.0034	6.0984	−.0014
	159.997	6.1008	+.0005	6.1013	+.0015
Even temperature 160°.	Mean value of pressure at 160° = P_m = 6.0998 atm.				
April 2, 1932	169.994	7.8182	+0.0011	7.8193	+0.0015
	169.993	7.8182	+.0013	7.8195	+.0017
	169.994	7.8182	+.0011	7.8193	+.0015
April 5, 1932	170.016	7.8183	−.0030	7.8153	−.0025
April 7, 1932	169.993	7.8147	+.0013	7.8160	−.0018
April 8, 1932	169.992	7.8140	+.0015	7.8155	−.0023
July 2, 1932	169.991	7.8159	+.0017	7.8176	−.0002
	169.981	7.8140	+.0036	7.8176	−.0002
	169.996	7.8168	+.0008	7.8176	−.0002
July 7, 1932	170.002	7.8174	−.0004	7.8170	−.0008
July 21, 1932	169.978	7.8148	+.0042	7.8190	+.0012
	169.996	7.8182	+.0008	7.8190	+.0012
	170.014	7.8216	−.0026	7.8190	+.0012
Even temperature 170°.	Mean value of pressure at 170° = P_m = 7.8178 atm.				

TABLE 1.—*Observed pressure of saturated water vapor*—Continued

Date	Observed quantities: Temperature θ_w	Observed quantities: Pressure P_w	Reduction to even temperature	Vapor pressure at even temperature P	Residual $P-P_m$
	°C. (*Int.*)		*Standard atmospheres* (*Int.*)		
April 2, 1932	180.024	9.9023	−0.0055	9.8968	+0.0010
	180.022	9.9011	−.0050	9.8961	+.0003
April 5, 1932	180.022	9.9017	−.0050	9.8967	+.0009
April 7, 1932	180.014	9.8990	−.0032	9.8958	.0000
April 8, 1932	180.001	9.8966	−.0002	9.8964	+.0006
July 7, 1932	179.999	9.8918	+.0002	9.8920	−.0038
	179.982	9.8926	+.0041	9.8967	+.0005
	179.969	9.8887	+.0071	9.8958	.0000
	179.996	9.8953	+.0009	9.8962	+.0004
Even temperature 180°.	Mean value of pressure at 180° = P_m = 9.8958 atm.				
April 2, 1932	190.001	12.3913	−0.0003	12.3910	+0.0023
	190.002	12.3904	−.0005	12.3899	+.0012
April 5, 1932	190.002	12.3905	−.0005	12.3900	+.0013
April 7, 1932	190.005	12.3890	−.0014	12.3876	−.0011
April 8, 1932	190.010	12.3908	−.0027	12.3881	−.0006
July 7, 1932	190.010	12.3898	−.0027	12.3871	−.0016
	190.010	12.3908	−.0027	12.3881	−.0006
	189.998	12.3871	+.0005	12.3876	−.0011
	190.012	12.3918	−.0033	12.3885	−.0002
Even temperature 190°.	Mean value of pressure at 190° = P_m = 12.3887 atm.				
March 25, 1932	200.141	15.3920	−0.0453	15.3467	−0.0005
March 28, 1932	199.957	15.3332	+.0138	15.3470	−.0002
March 29, 1932	200.037	15.3576	−.0119	15.3457	−.0015
March 30, 1932	199.700	15.2530	+.0963	15.3493	+.0021
April 1, 1932	199.935	15.3264	+.0209	15.3473	+.0001
April 7, 1932	199.990	15.3443	+.0032	15.3475	+.0003
April 8, 1932	199.712	15.2535	+.0924	15.3459	−.0013
July 7, 1932	199.996	15.3463	+.0013	15.3476	+.0004
	199.976	15.3395	+.0077	15.3472	.0000
	199.987	15.3440	+.0042	15.3482	+.0010
Even temperature 200°.	Mean value of pressure at 200° = P_m = 15.3472 atm.				
April 4, 1932	209.991	18.8256	+0.0034	18.8290	−0.0010
April 5, 1932	210.026	18.8393	−.0098	18.8295	−.0005
April 7, 1932	210.006	18.8314	−.0023	18.8291	−.0009
April 8, 1932	210.030	18.8424	−.0113	18.8311	+.0011
April 29, 1932	209.979	18.8245	+.0079	18.8324	+.0024
July 7, 1932	209.979	18.8213	+.0079	18.8292	−.0008
	209.957	18.8133	+.0162	18.8295	−.0005
	209.994	18.8277	+.0023	18.8300	.0000
Even temperature 210°.	Mean value of pressure at 210° = P_m = 18.8300 atm.				
April 4, 1932	219.998	22.8960	+0.0009	22.8969	+0.0005
April 5, 1932	220.002	22.8963	−.0009	22.8954	−.0010
April 7, 1932	220.003	22.8960	−.0013	22.8947	−.0017
April 8, 1932	220.013	22.9006	−.0057	22.8949	−.0015
April 29, 1932	219.993	22.8948	+.0031	22.8979	+.0015
July 7, 1932	219.999	22.8963	+.0004	22.8967	+.0003
	219.977	22.8867	+.0101	22.8968	+.0004
	219.996	22.8960	+.0018	22.8978	+.0014
Even temperature 220°.	Mean value of pressure at 220° = P_m = 22.8964 atm.				
April 4, 1932	230.007	27.6156	−0.0036	27.6120	+0.0003
April 5, 1932	230.019	27.6187	−.0096	27.6091	−.0026
April 7, 1932	230.015	27.6208	−.0076	27.6132	+.0015
April 8, 1932	230.010	27.6137	−.0051	27.6086	−.0031
April 29, 1932	230.006	27.6160	−.0030	27.6130	+.0013
July 7, 1932	229.986	27.6055	+.0071	27.6126	+.0009
	229.951	27.5883	+.0248	27.6131	+.0014
	229.999	27.6115	+.0005	27.6120	+.0003
Even temperature 230°.	Mean value of pressure at 230° = P_m = 27.6117 atm.				
April 4, 1932	240.014	33.0550	−0.0081	33.0469	+0.0053
April 5, 1932	240.060	33.0706	−.0349	33.0357	−.0059
April 7, 1932	240.015	33.0474	−.0087	33.0387	−.0029
April 8, 1932	240.021	33.0499	−.0122	33.0377	−.0039
April 29, 1932	240.026	33.0575	−.0151	33.0424	+.0008
July 8, 1932	239.976	33.0307	+.0139	33.0446	+.0030
	239.955	33.0188	+.0261	33.0449	+.0033
Even temperature 240°.	Mean value of pressure at 240° − P_m − 33.0146 atm.				

TABLE 1.—*Observed pressure of saturated water vapor*—Continued

Date	Observed quantities: Temperature θ_w	Observed quantities: Pressure P_w	Reduction to even temperature	Vapor pressure at even temperature P	Residual $P-P_w$
	°C. (*Int.*)	*Standard atmospheres* (*Int.*)			
March 25, 1932	250.186	39.3760	−0.1233	39.2527	−0.0039
March 28, 1932	250.026	39.2729	−.0172	39.2557	−.0009
March 29, 1932	249.968	39.2340	+.0212	39.2552	−.0014
March 30, 1932	249.832	39.1476	+.1114	39.2590	+.0024
April 1, 1932	250.131	39.3401	−.0869	39.2532	−.0034
April 7, 1932	250.030	39.2729	−.0199	39.2530	−.0036
April 8, 1932	250.005	39.2660	−.0033	39.2627	+.0061
July 8, 1932	249.977	39.2403	+.0153	39.2556	−.0010
	249.933	39.2148	+.0444	39.2592	+.0026
	249.985	39.2497	+.0099	39.2596	+.0030
Even temperature 250°.	Mean value of pressure at 250° = P_w = 39.2566 atm.				
March 28, 1932	259.991	46.3170	+0.0068	46.3238	−0.0048
April 4, 1932	259.999	46.3287	+.0008	46.3295	+.0009
April 5, 1932	260.011	46.3334	−.0083	46.3251	−.0035
April 7, 1932	260.010	46.3326	−.0075	46.3251	−.0035
April 8, 1932	260.005	46.3367	−.0038	46.3329	+.0043
April 29, 1932	259.998	46.3244	+.0015	46.3259	−.0027
July 8, 1932	259.986	46.3200	+.0105	46.3305	+.0019
	259.970	46.3086	+.0226	46.3312	+.0026
	259.997	46.3310	+.0023	46.3333	+.0047
Even temperature 260°.	Mean value of pressure at 260° = P_w = 46.3286 atm.				
March 28, 1932	269.996	54.3349	+0.0034	54.3383	+0.0050
April 4, 1932	270.000	54.3318	.0000	54.3318	−.0015
April 5, 1932	270.030	54.3533	−.0255	54.3278	−.0065
April 7, 1932	270.018	54.3454	−.0153	54.3301	−.0032
April 8, 1932	269.986	54.3193	+.0119	54.3312	−.0021
April 26, 1932	269.994	54.3305	+.0051	54.3356	+.0023
	270.002	54.3337	−.0017	54.3320	−.0013
April 28, 1932	269.990	54.3245	+.0085	54.3330	−.0003
	270.002	54.3325	−.0017	54.3308	−.0025
April 29, 1932	269.994	54.3303	+.0051	54.3354	+.0021
July 8, 1932	269.990	54.3286	+.0085	54.3371	+.0038
	269.975	54.3138	+.0213	54.3351	+.0018
	269.995	54.3302	+.0043	54.3345	+.0012
Even temperature 270°.	Mean value of pressure at 270° = P_w = 54.3333 atm.				
April 4, 1932	275.059	58.7648	−0.0532	58.7116	−0.0009
April 5, 1932	275.415	59.0855	−.3756	58.7099	−.0026
April 7, 1932	275.015	58.7218	−.0135	58.7083	−.0042
April 8, 1932	275.659	59.3127	−.6041	58.7086	−.0039
July 8, 1932	274.990	58.7073	+.0090	58.7163	+.0038
	274.968	58.6857	+.0289	58.7146	+.0021
	274.963	58.6820	+.0334	58.7154	+.0029
	274.998	58.7132	+.0018	58.7150	+.0025
Even temperature 275°.	Mean value of pressure at 275° = P_w = 58.7125 atm.				
March 28, 1932	280.015	63.3688	−0.0143	63.3545	−0.0013
April 4, 1932	280.009	63.3635	−.0086	63.3545	−.0013
April 5, 1932	280.219	63.5622	−.2093	63.3529	−.0029
April 7, 1932	280.054	63.4020	−.0516	63.3504	−.0054
April 8, 1932	279.996	63.3651	+.0038	63.3689	+.0131
April 26, 1932	280.098	63.4445	−.0937	63.3508	−.0050
April 29, 1932	280.005	63.3602	−.0048	63.3554	−.0004
July 8, 1932	279.988	63.3444	+.0115	63.3559	+.0001
	279.962	63.3214	+.0363	63.3577	+.0019
	279.988	63.3458	+.0115	63.3573	+.0015
Even temperature 280°.	Mean value of pressure at 280° = P_w = 63.3558 atm.				
March 28, 1932	290.406	73.9146	−0.4351	73.4795	+0.0016
April 4, 1932	290.027	73.5075	−.0289	73.4786	+.0007
April 5, 1932	290.027	73.5066	−.0289	73.4777	−.0002
April 7, 1932	290.001	73.4771	−.0011	73.4760	−.0019
April 8, 1932	290.009	73.4944	−.0096	73.4848	+.0069
April 26, 1932	290.014	73.4824	−.0150	73.4674	−.0105
	290.023	73.4963	−.0246	73.4717	−.0062
April 29, 1932	290.040	73.5189	−.0428	73.4761	−.0018
July 8, 1932	289.986	73.4657	+.0150	73.4807	+.0028
	289.949	73.4254	+.0546	73.4800	+.0021
	289.996	73.4796	+.0043	73.4839	+.0060
Even temperature 290°.	Mean value of pressure at 290° = P_w = 73.4779 atm.				

TABLE 1.—*Observed pressure of saturated water vapor*—Continued

Date	Observed quantities: Temperature θ_w	Observed quantities: Pressure P_w	Reduction to even temperature	Vapor pressure at even temperature P	Residual $P-P_m$
	°C. (*Int.*)		*Standard atmospheres (Int.)*		
March 25, 1932	300.129	84.9464	−0.1546	84.7918	−0.0051
March 28, 1932	300.005	84.8075	−.0060	84.8015	+.0046
March 29, 1932	299.970	84.7592	+.0358	84.7950	−.0019
March 30, 1932	299.953	84.7475	+.0561	84.8036	+.0067
April 1, 1932	300.048	84.8578	−.0573	84.8005	+.0036
April 7, 1932	300.047	84.8492	−.0561	84.7931	−.0038
April 8, 1932	300.025	84.8232	−.0299	84.7933	−.0036
June 30, 1932	299.609	84.3244	+.4665	84.7909	−.0060
	299.954	84.7441	+.0549	84.7990	+.0021
	299.813	84.5766	+.2234	84.8000	+.0031
July 1, 1932	299.654	84.3803	+.4128	84.7931	−.0038
July 8, 1932	300.009	84.8095	−.0107	84.7988	+.0019
	299.974	84.7671	+.0311	84.7982	+.0013
	299.973	84.7662	+.0322	84.7984	+.0015
	300.012	84.8111	−.0143	84.7968	−.0001
Even temperature 300°.	Mean value of pressure at 300° = P_m = 84.7969 atm.				
March 28, 1932	310.019	97.4298	−0.0253	97.4045	−0.0017
April 4, 1932	310.039	97.4615	−.0518	97.4097	+.0035
April 5, 1932	310.036	97.4503	−.0478	97.4025	−.0037
April 7, 1932	309.980	97.3822	+.0266	97.4088	+.0026
April 8, 1932	309.902	97.2816	+.1302	97.4118	+.0056
April 25, 1932	310.015	97.4259	−.0199	97.4060	−.0002
	310.015	97.4246	−.0199	97.4047	−.0015
	310.017	97.4264	−.0226	97.4038	−.0024
April 29, 1932	310.030	97.4361	−.0399	97.3962	−.0100
July 1, 1932	309.975	97.3685	+.0332	97.4017	−.0035
July 11, 1932	309.993	97.4006	+.0093	97.4099	+.0037
	309.973	97.3753	+.0359	97.4112	+.0050
	309.989	97.3949	+.0146	97.4095	+.0033
Even temperature 310°.	Mean value of pressure at 310° = P_m = 97.4062 atm.				
April 4, 1932	320.070	111.524	−0.103	111.421	+0.003
April 5, 1932	320.032	111.473	−.047	111.426	+.008
April 7, 1932	320.045	111.493	−.066	111.427	+.009
April 8, 1932	320.020	111.460	−.030	111.430	+.012
April 29, 1932	320.017	111.447	−.025	111.422	+.004
July 1, 1932	320.007	111.426	−.010	111.416	−.002
	320.007	111.422	−.010	111.412	−.006
	319.957	111.333	+.063	111.396	−.022
July 11, 1932	320.012	111.418	−.018	111.400	−.018
	320.017	111.446	−.025	111.421	+.003
	319.994	111.415	+.009	111.424	+.006
	320.003	111.425	−.004	111.421	+.003
Even temperature 320°.	Mean value of pressure at 320° = P_m = 111.418 atm.				
April 4, 1932	325.025	119.033	−0.039	118.994	+0.006
April 5, 1932	325.033	119.043	−.051	118.992	+.004
April 7, 1932	325.004	118.994	−.006	118.988	.000
April 8, 1932	325.004	118.998	−.006	118.992	+.004
July 1, 1932	324.968	118.920	+.050	118.970	−.018
	324.923	118.854	+.120	118.974	−.014
July 11, 1932	325.005	119.004	−.008	118.996	+.008
	324.997	119.986	+.005	118.991	+.003
	325.038	119.052	−.060	118.992	+.004
Even temperature 325°.	Mean value of pressure at 325° = P_m = 118.988 atm.				
April 4, 1932	330.020	126.994	−0.033	126.961	+0.001
April 5, 1932	330.010	126.980	−.016	126.964	+.004
April 7, 1932	330.009	126.983	−.015	126.968	+.008
April 8, 1932	330.012	126.988	−.020	126.968	+.008
April 26, 1932	330.020	126.990	−.033	126.957	−.003
	330.033	127.008	−.054	126.954	−.006
	330.038	127.012	−.062	126.950	−.010
April 29, 1932	330.043	127.030	−.070	126.960	.000
July 11, 1932	330.026	127.002	−.042	126.960	.000
	330.014	127.982	−.023	126.959	−.001
	330.032	127.005	−.052	126.953	−.007
	330.025	127.004	−.041	126.963	+.003
Even temperature 330°.	Mean value of pressure at 330° = P_m = 126.960 atm.				

TABLE 1.—*Observed pressure of saturated water vapor*—Continued

Date	Observed quantities: Temperature θ_w	Observed quantities: Pressure P_w	Reduction to even temperature	Vapor pressure at even temperature P	Residual $P-P_m$
	°C. (*Int.*)		*Standard atmospheres* (*Int.*)		
April 4, 1932	340.035	144.229	−0.063	144.166	−0.001
April 5, 1932	340.040	144.243	−.072	144.171	+.004
April 7, 1932	340.041	144.231	−.074	144.157	−.010
April 8, 1932	340.015	144.197	−.027	144.170	+.003
April 28, 1932	340.021	144.208	−.038	144.170	+.003
	340.025	144.204	−.045	144.159	−.008
April 29, 1932	340.028	144.213	−.051	144.162	−.005
July 11, 1932	340.026	144.216	−.047	144.169	+.002
	340.023	144.211	−.042	144.169	+.002
	339.994	144.161	+.011	144.172	+.005
	340.028	144.222	−.051	144.171	+.004
Even temperature 340°.	Mean value of pressure at 340° = P_m = 144.167 atm.				
March 29, 1932	349.998	163.208	+0.004	163.212	+.007
March 29, 1932	349.996	163.209	+.008	163.217	+.012
March 30, 1932	349.989	163.183	+.022	163.205	.009
	350.110	163.421	−.220	163.201	−.004
April 1, 1932	350.089	163.382	−.178	163.204	−.001
April 5, 1932	350.057	163.324	−.114	163.210	+.005
April 7, 1932	349.999	163.198	+.002	163.200	−.005
April 8, 1932	350.026	163.254	−.052	163.202	−.003
	350.043	163.282	−.086	163.196	−.009
	350.060	163.332	−.120	163.212	+.007
April 27, 1932	350.001	163.215	−.002	163.213	+.008
	350.018	163.225	−.036	163.189	−.016
July 11, 1932	350.027	163.262	−.054	163.208	+.003
	350.009	163.218	−.018	163.200	−.005
	350.020	163.246	−.040	163.206	+.001
July 12, 1932	350.025	163.254	−.050	163.204	−.001
	349.995	163.197	+.010	163.207	+.002
	350.006	163.214	−.012	163.202	−.003
Even temperature 350°.	Mean value of pressure at 350° = P_m = 163.205 atm.				
July 12, 1932	355.037	173.552	−0.078	173.474	+0.001
	355.006	173.475	−.013	173.462	−.011
	355.022	173.521	−.046	173.475	+.002
July 13, 1932	354.988	173.449	+.025	173.474	+.001
	354.966	173.402	+.072	173.474	+.001
	355.013	173.507	−.027	173.480	+.007
Even temperature 355°.	Mean value of pressure at 355° = P_m = 173.473 atm.				
April 29, 1932	360.008	184.311	−0.018	184.293	−0.004
July 12, 1932	360.029	184.365	−.064	184.301	+.004
	359.996	184.291	+.009	184.300	+.003
	360.004	184.308	−.009	184.299	+.002
July 13, 1932	359.976	184.241	+.053	184.294	−.003
	359.959	184.208	+.091	184.299	+.002
	359.996	184.285	+.009	184.294	−.003
Even temperature 360°.	Mean value of pressure at 360° = P_m = 184.297 atm.				
July 12, 1932	361.993	188.770	+0.016	188.786	−0.001
	361.990	188.765	+.023	188.788	+.001
	361.973	188.729	+.061	188.790	+.003
	362.007	188.803	−.016	188.787	.000
July 13, 1932	361.981	188.741	+.043	188.784	−.003
	361.965	188.708	+.079	188.787	.000
	361.992	188.770	+.018	188.788	+.001
Even temperature 362°.	Mean value of pressure at 362° = P_m = 188.787 atm.				
July 12, 1932	363.996	193.367	+0.009	193.376	−0.002
	363.978	193.323	+.051	193.374	−.004
	364.009	193.401	−.021	193.380	+.002
July 13, 1932	363.972	193.314	+.065	193.379	+.001
	363.958	193.282	+.097	193.379	+.001
	363.981	193.338	+.044	193.382	+.004
Even temperature 364°.	Mean value of pressure at 364° = P_m = 193.378 atm.				

TABLE 1.—*Observed pressure of saturated water vapor*—Continued.

Date	Observed quantities: Temperature θ_w	Observed quantities: Pressure P_w	Reduction to even temperature	Vapor pressure at even temperature P	Residual $P-P_m$
	°C. (Int.)	Standard atmospheres (Int.)			
July 12, 1932	366.019	198.110	−0.045	198.065	+0.001
	365.992	198.038	+.019	198.057	−.007
	366.032	198.139	−.076	198.063	−.001
	366.034	198.143	−.081	198.062	−.002
	366.022	198.119	−.052	198.067	+.003
July 13, 1932	365.951	197.949	+.116	198.065	+.001
	365.938	197.917	+.147	198.064	.000
	366.004	198.078	−.009	198.069	+.005
Even temperature 366°.	Mean value of pressure at 366° = P_m = 198.064 atm.				
July 13, 1932	368.099	202.876	−0.022	202.854	−0.003
	367.988	202.831	+.029	202.860	+.003
	368.030	202.938	−.073	202.865	+.008
	368.047	202.972	−.114	202.858	+.001
July 14, 1932	368.040	202.947	−.097	202.850	−.007
	368.018	202.899	−.044	202.855	−.002
Even temperature 368°.	Mean value of pressure at 368° = P_m = 202.857 atm.				
Apr. 29 1932	370.014	207.801	−0.035	207.766	−0.005
	370.009	207.788	−.022	207.766	−.005
	370.010	207.792	−.025	207.767	−.004
	370.020	207.820	−.049	207.771	.000
	370.035	207.857	−.087	207.770	−.001
July 13, 1932	369.959	207.667	+.101	207.768	−.003
	370.017	207.829	−.042	207.787	+.016
	370.034	207.862	−.084	207.778	+.007
	370.013	207.810	−.032	207.778	+.007
	370.056	207.924	−.138	207.786	+.015
July 14, 1932	370.041	207.870	−.101	207.769	−.002
	370.012	207.804	−.030	207.774	+.003
	370.006	207.795	−.015	207.780	+.009
	369.983	207.723	+.042	207.765	−.006
	370.016	207.812	−.040	207.772	+.001
	370.010	207.789	−.025	207.764	−.007
	369.986	207.726	+.035	207.761	−.010
	370.017	207.808	−.042	207.766	−.005
	370.001	207.766	−.002	207.764	−.007
Even temperature 370°.	Mean value of pressure at 370° = P_m = 207.771 atm.				
July 14, 1932	370.952	210.147	+0.120	210.267	−0.003
	370.966	201.182	+.085	210.267	−.003
	371.091	210.511	−.227	210.284	+.014
	371.082	210.480	−.205	210.275	+.005
	371.046	210.389	−.115	210.274	+.004
	371.038	210.360	−.095	210.265	−.005
	371.015	210.315	−.037	210.278	+.008
	371.011	210.297	−.027	210.270	.000
July 15, 1932	370.953	210.149	+.117	210.266	−.004
	370.914	210.047	+.215	210.262	−.008
	370.900	210.022	+.250	210.272	+.002
	370.892	209.987	+.270	210.257	−.013
Even temperature 371°.	Mean value of pressure at 371° = P_m = 210.270 atm.				
July 15, 1932	371.993	212.780	+0.018	212.798	+0.003
	372.004	212.806	−.010	212.796	+.001
	372.027	212.866	−.068	212.798	+.003
	372.014	212.831	−.035	212.796	+.001
	372.020	212.848	−.051	212.797	+.002
	372.016	212.846	−.040	212.806	+.011
July 22, 1932	372.070	212.966	−.177	212.789	−.006
	372.072	213.074	−.182	212.792	−.003
	372.098	213.033	−.248	212.785	−.010
Even temperature 372°.	Mean value of pressure at 372° = P_m = 212.795 atm.				
July 15, 1932	373.012	215.393	−0.031	215.362	−0.001
	373.012	215.391	−.031	215.360	−.003
	373.003	215.373	−.008	215.365	+.002
	373.005	215.367	−.013	215.354	−.009
	372.987	215.330	+.033	215.363	.000
	372.983	215.318	+.043	215.361	−.002
	372.974	215.294	+.066	215.360	−.003
	372.974	215.299	+.066	215.365	+.002
	372.996	215.361	+.010	215.371	+.008
July 22, 1932	373.059	215.515	−.151	215.364	+.001
	373.029	215.447	−.074	215.373	+.010
	373.008	215.381	−.020	215.361	−.002
Even temperature 373°.	Mean value of pressure at 373° = P_m = 215.363 atm.				

TABLE 1.—*Observed pressure of saturated water vapor*—Continued

Date	Observed quantities: Temperature θ_w	Observed quantities: Pressure P_w	Reduction to even temperature	Vapor pressure at even temperature P	Residual $P-P_m$
	°C. (Int.)		Standard atmospheres (Int.)		
July 22, 1932	374.001	217.985	−0.003	217.982	−0.003
	373.998	217.980	+.005	217.985	.000
	373.992	217.956	+.021	217.977	−.008
	373.999	217.971	+.003	217.974	−.011
	373.978	217.913	+.057	217.970	−.015
	373.957	217.859	+.111	217.970	−.015
July 25, 1932	374.039	218.091	−.101	217.990	+.005
	373.971	217.912	+.078	217.990	+.005
	373.948	217.855	+.134	217.989	+.004
	374.037	218.090	−.096	217.994	+.009
	374.052	218.135	−.134	218.001	+.016
	374.044	218.106	−.114	217.992	+.007
	374.069	218.169	−.178	217.991	+.006

Even temperature 374°. Mean value of pressure at 374° = P_m = 217.985 atm.

V. FORMULATION OF RESULTS

Proceeding with the mean values of vapor pressure corresponding to even temperatures assembled in Table 1 as described above, the next step was to express the aggregate result of the entire series by

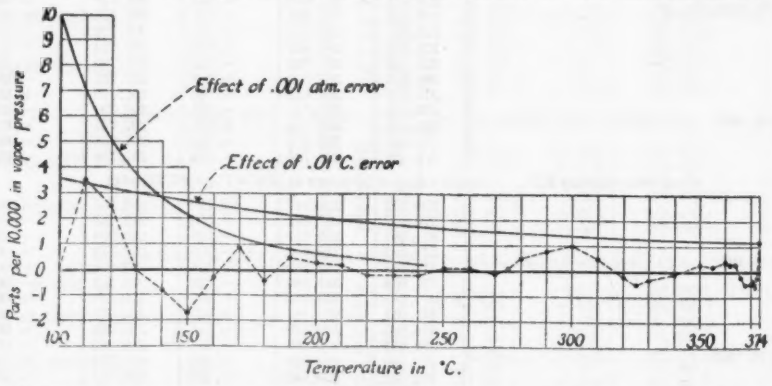


FIGURE 5.—*Deviation of mean observed pressures from the Bureau of Standards formulation*

means of a formula in order to smooth out irregularities caused by accidental errors of observation, and to provide a trustworthy method for interpolating intermediate values and for obtaining the derivative. The results of this formulation are given in Table 2. The constants of the empirical equation were determined by the method of least squares. Since the pressure at the 100° point is fixed by definition, the formula was made to give the value of exactly 1 atmosphere at this point. It was found necessary to apply the formula over two overlapping temperature ranges in order to secure a satisfactory fit.

The agreement of the formula with observation is shown by the differences in columns 4 and 5 and graphically in Figure 5. Since these differences in no case exceed the amount which experimental errors might cause, the formula is taken as a reliable representation of the aggregate results of the complete series of measurements. This formulation is the basis of a mutually consistent group of tables suitable for use as actual working tables. They are expressed in various appropriate units and arranged in convenient form to provide for intercomparison of current steam tables. The number of significant figures retained may be more than corresponds to the absolute accuracy of measurement, yet was determined by considerations of consistency and precision of formulation, calculation, conversion of units, and comparisons. The derivative is included because this factor is important for making thermodynamic correlations and for interpolating intermediate values.

For the units which involve the value of the intensity of gravity the internationally accepted value of 980.665 cm/sec.^{2} or its equivalent in the English system (32.174 ft./sec.^{2}) has been used. Obviously it would be undesirable to complicate the tabulation further by taking into account the difference of gravity in different localities. It may be regarded as unfortunate that existing engineering practice still retains pressure units which involve local values of gravity, particularly since the difference is usually so small that the change to standard gravity could be made painlessly.

It should not be overlooked that the temperatures given in this group of tables are expressed either on the international centigrade scale or on the Fahrenheit scale derived from it. For correlations involving the second law of thermodynamics, the departure of this temperature scale from the absolute or thermodynamic scale must be taken into account if it should be found to be significant.

Table 3 contains the values of the pressure of saturated water vapor and the derivative with respect to temperature at each ° C. from 100° to 374°. Values are given in each of the three units of pressure which are ordinarily used with the centigrade scale. The standard atmosphere is the standard international unit which has been used as the basis of reduction of the measurements. The centibar is a decimal subdivision of an internationally recognized unit of pressure.[9] This unit possesses several advantages for use as a practical working standard. It is derived directly from the fundamental units of length, mass, and time independently of the properties of any substance or of the intensity of gravity. It may therefore be used in thermodynamic calculations with other current cgs units without requiring a conversion factor, a property possessed by no system of thermodynamic units used in current steam tables. This unit is of convenient size for practical use and has a convenient and unequivocal name, which is a unique combination.

[9] The bar, equal to 10^6 dynes/cm^2 was approved as a unit of pressure by the International Meteorological Commission, Rome, 1913.

TABLE 2.—*Saturation pressure of water vapor*

[Results and formulation of observations]

Temperature	Saturation pressure		Deviations		Derivative [2]
θ	Mean observed P_m	Calculated [1] P	P_m-P	$\frac{P_m-P}{P}\times 10^4$	Calculated $dP/d\theta$
° C.	*Standard atmospheres (Int.)*			*Parts in 10,000*	*Atm./° C.*
100					0.03569
110	1.4143	1.4138	+0.0005	+3.5	.04750
120	1.9598	1.9593	+.0005	+2.5	.06208
130	2.6658	2.6658	.0000	.0	.07978
140	3.5661	3.5664	−.0003	−.8	.10095
150	4.6969	4.6977	−.0008	−1.7	.12598
160	6.0998	6.1000	−.0002	−.3	.15521
170	7.8178	7.8171	+.0007	+.9	.18899
180	9.8958	9.8962	−.0004	−.4	.22768
190	12.3887	12.3881	+.0006	+.5	.27161
200	15.3472	15.3468	+.0004	+.3	.32110
210	18.8300	18.8296	+.0004	+.2	.37647
220	22.8964	22.8969	−.0005	−.2	.43805
230	27.6117	27.6122	−.0005	−.2	.5061
240	33.0416	33.0421	−.0005	−.2	.5810
250	39.2566	39.2563	+.0003	+.1	.6630
260	46.3286	46.3280	+.0006	+.1	.7526
270	54.3333	54.3339	−.0006	−.1	.8500
275	58.7125	58.7122	+.0003	+.1	.9016
280	63.3558	63.3529	+.0029	+.5	.9553
290	73.4779	73.4723	+.0056	+.8	1.0701
300	84.7969	84.7881	+.0088	+1.0	1.1947
310	97.4062	97.4015	+.0047	+.5	1.3297
320	111.418	111.420	−.002	−.2	1.4760
325	118.988	118.994	−.006	−.5	1.5538
330	126.960	126.964	−.004	−.3	1.6349
340	144.167	144.168	−.001	−.1	1.8086
350	163.205	163.200	+.005	+.3	2.0016
355	173.473	173.470	+.003	+.2	2.1076
360	184.297	184.290	+.007	+.4	2.2220
362	188.787	188.782	+.005	+.3	2.2705
364	193.378	193.373	+.005	+.3	2.3208
366	198.064	198.067	−.003	−.2	2.3732
368	202.857	202.867	−.010	−.5	2.4277
370	207.771	207.781	−.010	−.5	2.4846
371	210.270	210.279	−.009	−.4	2.5141
372	212.795	212.808	−.013	−.6	2.5442
373	215.363	215.367	−.004	−.2	2.5751
374	217.985	217.958	+.027	+1.2	2.6068

[1] Calculated from the equation

$$\Theta \log_{10} P = a\Theta + b + cx^2 + dx^4 + ex^6$$

where a, b, c, d, and e are constants given in the table below for the two temperature ranges, $\Theta = (273.1+\theta)$, and $x = \left(\frac{\Theta^2}{298{,}000} - 1\right)$.

[2] Calculated from the equation

$$\frac{dP}{d\Theta} = 2.302585P\left(\frac{a - \log_{10} P}{\Theta} + 6cx^2 + 10dx^4 + 12ex^5\right)$$

which is the derivative of the above equation, using the same notation and constants.

Table of constants

	Range 100°–275° C.	Range 275°–374° C.
$a=$	+5.4247285	+5.4231165
$b=$	−2003.853	−2002.971
$c=$	+87.880	+109.54
$d=$	+107.35	−608.22
$e=$	−96.252	+1399.0

TABLE 3.—*Pressure of saturated water vapor*

[1 standard atmosphere = 101.325 centibars = 1.033228 kg/cm [1].] [2]

Temperature θ	Pressure P	Derivative $dP/d\theta$	Pressure P	Derivative $dP/d\theta$	Pressure P	Derivative $dP/d\theta$	Temperature θ
°C. (*Int.*)	*Std. Atm.*	*Std. Atm. per °C.*	*Centibars*	*Centibars per °C.*	*kg/cm²*	*kg/cm² per °C.*	°C. (*Int.*)
100	1.0000	0.03569	101.325	3.616	1.03323	0.03688	100
101	1.0362	.03676	104.99	3.725	1.0706	.03798	101
102	1.0735	.03785	108.77	3.835	1.1092	.03911	102
103	1.1119	.03896	112.66	3.948	1.1488	.04025	103
104	1.1515	.04011	116.68	4.064	1.1898	.04144	104
105	1.1922	.04128	120.80	4.183	1.23188	.04265	105
106	1.2341	.04247	125.05	4.303	1.2751	.04388	106
107	1.2771	.04369	129.40	4.427	1.3195	.04514	107
108	1.3214	.04493	133.89	4.553	1.3653	.04642	108
109	1.3670	.04621	138.51	4.682	1.4124	.04775	109
110	1.4138	.04750	143.25	4.813	1.4608	.04908	110
111	1.4620	.04883	148.14	4.948	1.5106	.05045	111
112	1.5115	.05019	153.15	5.086	1.5617	.05186	112
113	1.5624	.05157	158.31	5.225	1.6143	.05328	113
114	1.6146	.05298	163.60	5.368	1.6682	.05474	114
115	1.6683	.05442	169.04	5.514	1.7237	.05623	115
116	1.7235	.05590	174.63	5.664	1.7808	.05776	116
117	1.7802	.05740	180.38	5.816	1.8394	.05931	117
118	1.8383	.05893	186.27	5.971	1.8994	.06089	118
119	1.8980	.06049	192.31	6.129	1.9611	.06250	119
120	1.9593	.06208	198.53	6.290	2.0244	.06414	120
121	2.0222	.06370	204.90	6.454	2.0894	.06582	121
122	2.0867	.06536	211.43	6.623	2.1560	.06753	122
123	2.1529	.06704	218.14	6.793	2.2244	.06927	123
124	2.2208	.06876	225.02	6.967	2.2946	.07104	124
125	2.2904	.07051	232.07	7.144	2.3665	.07285	125
126	2.3619	.07230	239.32	7.326	2.4404	.07470	126
127	2.4351	.07412	246.74	7.510	2.5160	.07658	127
128	2.5101	.07597	254.34	7.698	2.5935	.07849	128
129	2.5870	.07786	262.13	7.889	2.6730	.08045	129
130	2.6658	.07978	270.11	8.084	2.7544	.08243	130
131	2.7466	.08173	278.30	8.281	2.8379	.08445	131
132	2.8293	.08372	286.68	8.483	2.9233	.08650	132
133	2.9140	.08575	295.26	8.689	3.0108	.08860	133
134	3.0008	.08781	304.06	8.897	3.1005	.09073	134
135	3.0897	.08991	313.06	9.110	3.1924	.09290	135
136	3.1806	.09204	322.27	9.326	3.2863	.09510	136
137	3.2738	.09421	331.72	9.546	3.3826	.09734	137
138	3.3691	.09642	341.37	9.770	3.4810	.09962	138
139	3.4666	.09867	351.25	9.998	3.5818	.10195	139
140	3.5664	.10095	361.37	10.229	3.6849	.10430	140
141	3.6686	.10328	371.72	10.465	3.7905	.10671	141
142	3.7730	.10564	382.30	10.704	3.8984	.10915	142
143	3.8798	.10804	393.12	10.947	4.0087	.11163	143
144	3.9891	.11048	404.20	11.194	4.1216	.11415	144
145	4.1008	.11296	415.51	11.446	4.2371	.11671	145
146	4.2150	.11548	427.08	11.701	4.3551	.11932	146
147	4.3318	.11805	438.92	11.961	4.4757	.12197	147
148	4.4511	.12065	451.01	12.225	4.5990	.12466	148
149	4.5731	.12329	463.37	12.492	4.7251	.12739	149
150	4.6977	.12598	475.99	12.765	4.8538	.13017	150
151	4.8251	.12871	488.90	13.042	4.9854	.13299	151
152	4.9552	.13148	502.09	13.322	5.1199	.13585	152
153	5.0880	.13429	515.54	13.607	5.2571	.13875	153
154	5.2238	.13714	529.30	13.896	5.3974	.14170	154

[1] 1 centibar = 10,000 dyn/cm².
[2] Standard gravity = 980.665 cm/sec.²

TABLE 3.—*Pressure of saturated water vapor*—Continued

Temperature θ	Pressure P	Derivative $dP/d\theta$	Pressure P	Derivative $dP/d\theta$	Pressure P	Derivative $dP/d\theta$	Temperature θ
°C. (Int.)	Std. Atm.	Std. Atm. per °C.	Centibars	Centibars per °C.	kg/cm²	kg/cm² per °C.	°C. (Int.)
155	5.3623	.14004	543.34	14.190	5.5405	.14469	155
156	5.5039	.14298	557.68	14.487	5.6868	.14773	156
157	5.6483	.14597	572.31	14.790	5.8360	.15082	157
158	5.7959	.14901	587.27	15.098	5.9885	.15396	158
159	5.9464	.15209	602.52	15.411	6.1440	.15714	159
160	6.1000	.15521	618.08	15.727	6.3027	.16037	160
161	6.2568	.15837	633.97	16.047	6.4647	.16363	161
162	6.4168	.16159	650.18	16.373	6.6300	.16696	162
163	6.5800	.16485	666.72	16.703	6.7986	.17033	163
164	6.7465	.16816	683.59	17.039	6.9707	.17375	164
165	6.9163	.17151	700.79	17.378	7.1461	.17721	165
166	7.0895	.17491	718.34	17.723	7.3251	.18072	166
167	7.2661	.17836	736.24	18.072	7.5075	.18429	167
168	7.4462	.18185	754.49	18.426	7.6936	.18789	168
169	7.6298	.18540	773.09	18.786	7.8833	.19156	169
170	7.8171	.18899	792.07	19.149	8.0768	.19527	170
171	8.0079	.19263	811.40	19.518	8.2740	.19903	171
172	8.2023	.19632	831.10	19.892	8.4748	.20284	172
173	8.4005	.20007	851.18	20.272	8.6796	.20672	173
174	8.6025	.20386	871.65	20.656	8.8883	.21063	174
175	8.8083	.20770	892.50	21.045	9.1010	.21460	175
176	9.0179	.21159	913.74	21.439	9.3175	.21862	176
177	9.2315	.21554	935.38	21.840	9.5382	.22270	177
178	9.4490	.21953	957.42	22.244	9.7630	.22682	178
179	9.6705	.22357	979.86	22.653	9.9918	.23100	179
180	9.8962	.22768	1,002.7	23.070	10.225	.23525	180
181	10.126	.23183	1,026.0	23.490	10.462	.23953	181
182	10.360	.23604	1,049.7	23.917	10.704	.24388	182
183	10.598	.24029	1,073.8	24.347	10.950	.24827	183
184	10.840	.24460	1,098.4	24.784	11.200	.25273	184
185	11.087	.24896	1,123.4	25.226	11.455	.25723	185
186	11.338	.25338	1,148.8	25.674	11.715	.26180	186
187	11.594	.25786	1,174.8	26.128	11.979	.26643	187
188	11.854	.26238	1,201.1	26.586	12.248	.27110	188
189	12.119	.26697	1,228.0	27.051	12.522	.27584	189
190	12.388	.27161	1,255.2	27.521	12.800	.28064	190
191	12.662	.27630	1,283.0	27.996	13.083	.28548	191
192	12.941	.28105	1,311.2	28.477	13.371	.29039	192
193	13.224	.28585	1,339.9	28.964	13.663	.29535	913
194	13.512	.29071	1,369.1	29.456	13.961	.30037	194
195	13.806	.29564	1,398.9	29.956	14.265	.30546	195
196	14.104	.30061	1,429.1	30.459	14.573	.31060	196
197	14.407	.30564	1,459.8	30.969	14.886	.31580	197
198	14.715	.31074	1,491.0	31.486	15.204	.32107	198
199	15.028	.31589	1,522.7	32.008	15.527	.32639	199
200	15.347	.32110	1,555.0	32.535	15.857	.33177	200
201	15.671	.32637	1,587.9	33.069	16.192	.33721	201
202	16.000	.33169	1,621.2	33.608	16.532	.34271	202
203	16.334	.33708	1,655.0	34.155	16.877	.34828	203
204	16.674	.34252	1,689.5	34.706	17.228	.35390	204
205	17.019	.34803	1,724.5	35.264	17.585	.35959	205
206	17.370	.35360	1,760.0	35.829	17.947	.36535	206
207	17.726	.35922	1,796.1	36.398	18.315	.37116	207
208	18.088	.36491	1,832.8	36.975	18.689	.37704	208
209	18.456	.37066	1,870.1	37.557	19.069	.38298	209
210	18.830	.37647	1,907.9	38.146	19.456	.38898	210
211	19.209	.38235	1,946.4	38.742	19.847	.39505	211
212	19.594	.38828	1,985.4	39.342	20.245	.40118	212
213	19.986	.39428	2,025.1	39.950	20.650	.40738	213
214	20.383	.40034	2,065.3	40.564	21.060	.41364	214
215	20.786	.40646	2,106.1	41.185	21.477	.41997	215
216	21.196	.41265	2,147.7	41.812	21.900	.42636	216
217	21.612	.41890	2,189.8	42.445	22.330	.43282	217
218	22.034	.42522	2,232.6	43.085	22.766	.43935	218
219	22.462	.43160	2,276.0	43.732	23.208	.44594	219

TABLE 3.—*Pressure of saturated water vapor*—Continued

Temperature θ	Pressure P	Derivative $dP/d\theta$	Pressure P	Derivative $dP/d\theta$	Pressure P	Derivative $dP/d\theta$	Temperature θ
°C. (*Int.*)	*Std. Atm.*	*Std. Atm. per °C.*	*Centibars*	*Centibars per °C.*	*kg/cm²*	*kg/cm² per °C.*	°C. (*Int.*)
220	22.897	.43805	2,320.0	44.385	23.658	.45261	220
221	23.338	.44455	2,364.7	45.044	24.113	.45932	221
222	23.786	.45113	2,410.1	45.711	24.576	.46612	222
223	24.240	.45777	2,456.1	46.384	25.045	.47298	223
224	24.702	.46448	2,502.9	47.063	25.523	.47991	224
225	25.170	.47125	2,550.4	47.749	26.006	.48691	225
226	25.644	.47809	2,598.4	48.442	26.496	.49398	226
227	26.126	.48500	2,647.2	49.143	26.994	.5011	227
228	26.614	.49197	2,696.7	49.849	27.498	.5083	228
229	27.110	.49901	2,746.9	50.56	28,011	.5156	229
230	27.612	.5061	2,797.8	51.28	28.529	.5229	230
231	28.122	.5133	2,849.5	52.01	29.056	.5304	231
232	28.639	.5205	2,901.8	52.74	29.591	.5378	232
233	29.163	.5279	2,954.9	53.48	30.132	.5454	233
234	29.695	.5352	3,008.8	54.23	30.682	.5530	234
235	30.234	.5427	3063.5	54.99	31.239	.5607	235
236	30.780	.5502	3118.8	55.75	31.803	.5685	236
237	31.334	.5578	3174.9	56.52	32.375	.5763	237
238	31.896	.5655	3231.9	57.30	32.956	.5843	238
239	32.465	.5732	3289.5	58.08	33.544	.5923	239
240	33.042	.5810	3348.0	58.87	34.140	.6003	240
241	33.627	.5889	3407.3	59.67	34.744	.6085	241
242	34.220	.5968	3467.3	60.47	35.357	.6167	242
243	34.821	.6049	3528.2	61.29	35.978	.6250	243
244	35.430	.6130	3589.9	62.11	36.607	.6333	244
245	36.047	.6211	3652.5	62.93	37.245	.6418	245
246	36.672	.6293	3715.8	63.77	37.891	.6503	246
247	37.305	.6377	3779.9	64.61	38.545	.6589	247
248	37.947	.6460	3845.0	65.46	39.208	.6675	248
249	38.598	.6545	3910.9	66.32	39.881	.6763	249
250	39.256	.6630	3977.6	67.18	40.560	.6851	250
251	39.924	.6717	4045.3	68.06	41.251	.6940	251
252	40.600	.6803	4113.8	68.93	41.949	.7029	252
253	41.284	.6891	4183.1	69.82	42.656	.7120	253
254	41.978	.6979	4253.4	70.72	43.373	.7211	254
255	42.680	.7068	4324.6	71.62	44.098	.7303	255
256	43.392	.7158	4396.7	72.53	44.834	.7396	256
257	44.112	.7249	4469.6	73.45	45.578	.7490	257
258	44.841	.7340	4543.5	74.38	46.331	.7584	258
259	45.580	.7433	4618.4	75.31	47.095	.7680	259
260	46.328	.7526	4694.2	76.25	47.867	.7776	260
261	47.085	.7619	4770.9	77.20	48.650	.7873	261
262	47.852	.7714	4848.6	78.16	49.442	.7970	262
263	48.628	.7809	4927.2	79.13	50.244	.8069	263
264	49.414	.7906	5006.9	80.10	51.056	.8168	264
265	50.209	.8002	5087.4	81.08	51.877	.8268	265
266	51.014	.8100	5169.0	82.08	52.709	.8369	266
267	51.829	.8199	5251.6	83.08	53.551	.8471	267
268	52.654	.8298	5335.2	84.08	54.404	.8574	268
269	53.489	.8399	5419.8	85.10	55.266	.8678	269
270	54.334	.8500	5505.4	86.12	56.139	.8782	270
271	55.189	.8602	5592.0	87.16	57.023	.8887	271
272	56.054	.8704	5679.7	88.20	57.917	.8994	272
273	56.930	.8808	5768.4	89.25	58.822	.9101	273
274	57.816	.8912	5858.2	90.31	59.737	.9209	274
275	58.712	.9018	5949.0	91.37	60.663	.9317	275
276	59.619	.9120	6040.9	92.41	61.600	.9423	276
277	60.536	.9227	6133.8	93.49	62.547	.9533	277
278	61.464	.9335	6227.8	94.58	63.506	.9645	278
279	62.403	.9444	6323.0	95.69	64.477	.9757	279
280	63.353	.9553	6419.2	96.80	65.452	.9871	280
281	64.314	.9664	6516.6	97.92	66.451	.9985	281
282	65.286	.9775	6615.1	99.05	67.455	1.0100	282
283	66.269	.9888	6714.7	100.19	68.471	1.0216	283
284	67.263	1.0001	6815.4	101.34	69.498	1.0333	284

TABLE 3.—*Pressure of saturated water vapor*—Continued

Temperature θ	Pressure P	Derivative $dP/d\theta$	Pressure P	Derivative $dP/d\theta$	Pressure P	Derivative $dP/d\theta$	Temperature θ
°C. (*Int.*)	*Std. Atm.*	*Std. Atm. per °C.*	*Centibars*	*Centibars per °C.*	*kg/cm²*	*kg/cm² per °C.*	°C. (*Int.*)
285	68.269	1.0116	6917.4	102.50	70.537	1.0452	285
286	69.286	1.0231	7020.4	103.67	71.588	1.0571	286
287	70.315	1.0347	7124.7	104.84	72.651	1.0691	287
288	71.356	1.0464	7230.1	106.03	73.727	1.0812	288
289	72.408	1.0582	7336.7	107.22	74.814	1.0934	289
290	73.472	1.0701	7444.6	108.43	75.913	1.1057	290
291	74.548	1.0821	7553.6	109.64	77.025	1.1181	291
292	75.637	1.0942	7663.9	110.87	78.150	1.1306	292
293	76.737	1.1064	7775.4	112.11	79.287	1.1432	293
294	77.850	1.1188	7888.2	113.36	80.437	1.1560	294
295	78.974	1.1312	8002.0	114.62	81.598	1.1688	295
296	80.112	1.1437	8117.3	115.89	82.774	1.1817	296
297	81.262	1.1563	8233.9	117.16	83.962	1.1947	297
298	82.424	1.1690	8351.6	118.45	85.163	1.2078	298
299	83.600	1.1818	8470.8	119.75	86.378	1.2211	299
300	84.788	1.1947	8591.1	121.05	87.605	1.2344	300
301	85.989	1.2077	8712.8	122.37	88.846	1.2478	301
302	87.204	1.2209	8835.9	123.71	90.102	1.2615	302
303	88.431	1.2341	8960.3	125.05	91.369	1.2751	303
304	89.672	1.2474	9086.0	126.39	92.652	1.2888	304
305	90.926	1.2609	9,213.1	127.76	93.947	1.3028	305
306	92.194	1.2744	9,341.6	129.13	95.257	1.3167	306
307	93.475	1.2881	9,471.4	130.52	96.581	1.3309	307
308	94.770	1.3019	9,602.6	131.92	97.919	1.3452	308
309	96.079	1.3157	9,735.2	133.31	99.272	1.3594	309
310	97.402	1.3297	9,869.3	134.73	100.64	1.3739	310
311	98.738	1.3438	10,005	136.16	102.02	1.3885	311
312	100.09	1.3581	10,142	137.61	103.42	1.4032	312
313	101.45	1.3724	10,279	139.06	104.82	1.4180	313
314	102.83	1.3868	10,419	140.52	106.24	1.4329	314
315	104.23	1.4014	10,561	142.00	107.69	1.4480	315
316	105.64	1.4161	10,704	143.49	109.15	1.4632	316
317	107.06	1.4309	10,848	144.99	110.62	1.4784	317
318	108.50	1.4458	10,994	146.50	112.11	1.4938	318
319	109.95	1.4609	11,141	148.03	113.60	1.5094	319
320	111.42	1.4760	11,290	149.56	115.12	1.5250	320
321	112.90	1.4913	11,440	151.11	116.65	1.5409	321
322	114.40	1.5068	11,592	152.68	118.20	1.5569	322
323	115.92	1.5223	11,746	154.25	119.77	1.5729	323
324	117.45	1.5380	11,901	155.84	121.35	1.5891	324
325	118.99	1.5538	12,057	157.44	122.94	1.6054	325
326	120.55	1.5697	12,215	159.05	124.56	1.6219	326
327	122.13	1.5858	12,375	160.68	126.19	1.6385	327
328	123.73	1.6020	12,537	162.32	127.84	1.6552	328
329	125.34	1.6184	12,700	163.98	129.50	1,6722	329
330	126.96	1.6349	12,864	165.66	131.18	1.6892	330
331	128.61	1.6516	13,031	167.35	132.88	1.7065	331
332	130.27	1.6684	13,200	169.05	134.60	1.7238	332
333	131.94	1.6853	13,369	170.76	136.32	1.7413	333
334	133.64	1.7024	13,541	172.50	138.08	1.7590	334
335	135.35	1.7197	13,714	174.25	139.85	1.7768	335
336	137.08	1.7371	13,890	176.01	141.63	1.7948	336
337	138.82	1,7547	14,066	177.80	143.43	1.8130	337
338	140.59	1.7724	14,245	179.59	145.26	1.8313	338
339	142.37	1.7905	14,426	181.42	147.10	1,8500	339
340	144.17	1.8086	14,608	183.26	148.96	1.8687	340
341	145.98	1.8269	14,791	185.11	150.83	1.8876	341
342	147.82	1.8455	14,978	187.00	152.73	1.9068	342
343	149.68	1.8642	15,166	188.89	154.65	1.9261	343
344	151.55	1.8831	15,356	190.81	156.59	1.9457	344
345	153.44	1.9023	15,547	192.75	158.54	1.9655	345
346	155.36	1.9217	15,742	194.72	160.52	1.9856	346
347	157.29	1.9413	15,937	196.70	162.52	2.0058	347
348	159.24	1.9611	16,135	198.71	164.53	2.0263	348
349	161.21	1.9812	16,335	200.75	166.57	2.0470	349
350	163.20	2.0016	16,536	202.81	168.62	2.0681	350
351	165.21	2.0222	16,740	204.90	170.70	2.0894	351
352	167.24	2.0431	16,946	207.02	172.80	2.1110	352
353	169.30	2.0643	17,154	209.17	174.93	2.1329	353
354	171.37	2.0858	17,364	211.34	177.06	2.1551	354

TABLE 3.—*Pressure of saturated water vapor*—Continued

Temperature θ	Pressure P	Derivative $dP/d\theta$	Pressure P	Derivative $dP/d\theta$	Pressure P	Derivative $dP/d\theta$	Temperature θ
°C. (Int.)	Std. Atm.	Std. Atm. per °C.	Centibars	Centibars per °C.	kg/cm²	kg/cm² per °C.	°C. (Int.)
355	173.47	2.1076	17,577	213.55	179.23	2.1776	355
356	175.59	2.1298	17,792	215.80	181.42	2.2006	356
357	177.73	2.1523	18,008	218.08	183.64	2.2238	357
358	179.89	2.1751	18,227	220.39	185.87	2.2474	358
359	182.08	2.1984	18,449	222.75	188.13	2.2714	359
360	184.29	2.2220	18,673	225.14	190.41	2.2958	360
361	186.52	2.2460	18,899	227.58	192.72	2.3206	361
362	188.78	2.2705	19,128	230.06	195.05	2.3459	362
363	191.06	2.2954	19,359	232.58	197.41	2.3717	363
364	193.37	2.3208	19,593	235.16	199.80	2.3979	364
365	195.71	2.3467	19,830	237.78	202.21	2.4247	365
366	198.07	2.3732	20,069	240.46	204.65	2.4521	366
367	200.45	2.4001	20,311	243.19	207.11	2.4799	367
368	202.87	2.4277	20,556	245.99	209.61	2.5084	368
369	205.31	2.4558	20,803	248.83	212.13	2.5374	369
370	207.78	2.4846	21,053	251.75	214.68	2.5672	370
371	210.28	2.5141	21,307	254.74	217.27	2.5976	371
372	212.81	2.5442	21,563	257.79	219.88	2.6287	372
373	215.37	2.5751	21,822	260.92	222.53	2.6607	373
374	217.96	2.6068	22,085	264.13	225.20	2.6934	374

The kilogram per square centimeter has a wide usage, particularly abroad and in scientific circles. Its chief disadvantage is that the intensity of gravity must be specified to make the unit definite. A second is that, lacking a name, it has frequently been confused with the atmosphere, having approximately the same value. The three units are used coordinately in this table to facilitate their use interchangeably and give the user a choice of unit appropriate for his purpose.

Table 4 contains values of the pressure of saturated steam in pounds per square inch at each degree Fahrenheit. This pressure unit, like the kg/cm² is indefinite unless the intensity of gravity is specified. Table 5 contains values of the derivative in the corresponding units.

TABLE 4.—*Pressure of saturated water vapor*

[Pounds[1] per square inch]

Temperature °F.	0	1	2	3	4	5	6	7	8	9
θ	Pressure									
	Lbs./in.²	Lbs./in.²	Lbs./in.²	Lbs./in.²	Lbs./in.²	Lbs./in.²	Lbs./in.²	Lbs./in.²	Lbs./in.²	Lbs./in.²
210			14.696	14.990	15.288	15.592	15.900	16.213	16.532	16.857
220	17.186	17.521	17.862	18.206	18.556	18.911	19.273	19.640	20.014	20.393
230	20.777	21.167	21.565	21.969	22.377	22.793	23.215	23.642	24.076	24.518
240	24.966	25.420	25.882	26.349	26.824	27.305	27.795	28.290	28.794	29.305
250	29.823	30.348	30.877	31.420	31.969	32.525	33.088	33.660	34.243	34.829
260	35.425	36.028	36.641	37.262	37.892	38.530	39.177	39.834	40.498	41.172
270	41.853	42.545	43.246	43.957	44.677	45.406	46.144	46.892	47.651	48.419
280	49.198	49.986	50.784	51.593	52.412	53.243	54.063	54.933	55.793	56.665
290	57.549	58.444	59.349	60.266	61.194	62.133	63.085	64.046	65.020	66.006
300	67.006	68.015	69.038	70.074	71.120	72.181	73.251	74.336	75.433	76.546
310	77.669	78.805	79.957	81.119	82.296	83.484	84.691	85.909	87.141	88.386
320	89.646	90.922	92.209	93.514	94.829	96.162	97.510	98.873	100.25	101.64
330	103.05	104.47	105.91	107.36	108.84	110.32	111.83	113.34	114.88	116.43
340	118.00	119.58	121.18	122.80	124.44	126.09	127.76	129.45	131.15	132.87
350	134.62	136.37	138.15	139.94	141.75	143.58	145.44	147.31	149.19	151.10

[1] Standard gravity = 32.174 ft./sec.²

TABLE 4.—*Pressure of saturated water vapor*—Continued

Temperature ° F.	0	1	2	3	4	5	6	7	8	9
θ	Pressure									
	Lbs./in.[2]	*Lbs./in.*[2]	*Lbs./in.*[2]	*Lbs./in.*[2]	*Lbs./in.*[2]	*Lbs./in.*[2]	*Lbs./in.*[2]	*Lbs./in.*[2]	*Lbs./in.*[2]	*Lbs./in.*[2]
360	153.02	154.97	156.93	158.91	160.91	162.94	164.98	167.04	169.13	171.23
370	173.35	175.50	177.67	179.85	182.06	184.29	186.53	188.81	191.10	193.41
380	195.74	198.10	200.48	202.89	205.32	207.76	210.24	212.72	215.24	217.78
390	220.34	222.92	225.54	228.18	230.84	233.50	236.21	238.95	241.70	244.48
400	247.29	250.11	252.97	255.85	258.75	261.67	264.63	267.61	270.63	273.66
410	276.73	279.81	282.92	286.05	289.22	292.43	295.65	298.90	302.16	305.47
420	308.82	312.17	315.56	318.98	322.43	325.89	329.40	332.93	336.50	340.09
430	343.70	347.35	351.03	354.74	358.47	362.25	366.06	369.90	373.76	377.65
440	381.58	385.53	389.52	393.53	397.60	401.68	405.79	409.94	414.12	418.33
450	422.57	426.86	431.17	435.53	439.90	444.32	448.77	453.24	457.76	462.31
460	466.90	471.51	476.17	480.86	485.59	490.35	495.15	499.98	504.85	509.76
470	514.69	519.68	424.69	529.76	534.84	539.96	545.12	550.32	555.57	560.86
480	566.17	571.52	576.91	582.36	587.83	593.33	598.88	604.46	610.08	615.77
490	621.48	627.23	633.03	638.86	644.72	650.63	656.59	662.60	668.64	674.72
500	680.84	687.01	693.21	699.46	705.76	712.09	718.47	724.90	731.36	737.88
510	744.44	751.03	757.67	764.35	771.10	777.87	784.71	791.57	798.50	805.46
520	812.46	819.52	826.62	833.77	840.96	848.20	855.50	862.84	870.23	877.66
530	885.12	892.65	900.23	907.85	915.54	923.26	931.04	938.87	946.74	954.68
540	962.64	970.67	978.74	986.87	995.04	1,003.3	1,011.6	1,019.9	1,028.3	1,036.7
550	1,045.2	1,053.8	1,062.4	1,071.0	1,079.7	1,088.5	1,097.3	1,106.2	1,115.1	1,124.1
560	1,133.2	1,142.3	1,151.4	1,160.6	1,169.9	1,179.2	1,188.6	1,198.0	1,207.5	1,217.0
570	1,226.6	1,236.3	1,246.0	1,255.8	1,265.7	1,275.6	1,285.5	1,295.5	1,305.6	1,315.8
580	1,326.0	1,336.3	1,346.6	1,357.0	1,367.4	1,377.9	1,388.5	1,399.1	1,409.8	1,420.6
590	1,431.4	1,442.3	1,453.3	1,464.3	1,475.3	1,486.4	1,497.6	1,508.9	1,520.3	1,531.8
600	1,543.3	1,554.8	1,566.4	1,578.1	1,589.8	1,601.6	1,613.4	1,625.4	1,637.4	1,649.5
610	1,661.6	1,673.8	1,686.1	1,698.6	1,711.1	1,723.6	1,736.2	1,748.8	1,761.4	1,774.2
620	1,787.0	1,800.0	1,813.1	1,826.2	1,839.4	1,852.6	1,865.9	1,879.3	1,892.8	1,906.3
630	1,919.9	1,933.5	1,947.3	1,961.2	1,975.1	1,989.1	2,003.2	2,017.3	2,031.5	2,045.8
640	2,060.2	2,074.7	2,089.3	2,104.0	2,118.7	2,133.4	2,148.3	2,163.4	2,178.4	2,193.6
650	2,208.8	2,224.1	2,239.5	2,255.0	2,270.6	2,286.3	2,302.0	2,317.8	2,333.8	2,349.8
660	2,366.0	2,382.2	2,398.4	2,414.7	2,431.2	2,447.8	2,464.5	2,481.3	2,498.1	2,515.1
670	2,532.1	2,549.3	2,566.6	2,584.0	2,601.4	2,618.9	2,636.6	2,654.3	2,672.3	2,690.3
680	2,708.3	2,726.5	2,744.8	2,763.2	2,781.7	2,800.3	2,819.0	2,838.0	2,857.0	2,876.2
690	2,895.5	2,914.8	2,934.1	2,953.6	2,973.4	2,993.3	3,013.3	3,033.4	3,053.6	3,073.9
700	3,094.4	3,115.0	3,135.8	3,156.7	3,177.7	3,198.9				

TABLE 5.—*Derivative of the pressure of saturated water vapor* (dP/d)

[Pounds[1] per square inch per degree Fahrenheit]

Temperature θ	0	1	2	3	4	5	6	7	8	9
	Derivative									
° F.	*Lbs./in.*[2] ° F.	*Lbs./in.*[2] ° F.	*Lbs./in.*[2] ° F.	*Lbs./in.*[2] ° F.	*Lbs./in.*[2] ° F.	*Lbs./in.*[2] ° F.	*Lbs./in.*[2] ° F.	*Lbs./in.*[2] ° F.	*Lbs./in.*[2] ° F.	*Lbs./in.*[2] ° F.
210			0.2914	0.2962	0.3011	0.3061	0.3111	0.3161	0.3212	0.3264
220	0.3317	0.3370	.3424	.3478	.3534	.3590	.3646	.3703	.3761	.3819
230	.3878	.3938	.3999	.4061	.4123	.4186	.4249	.4313	.4378	.4443
240	.4511	.4578	.4646	.4714	.4783	.4854	.4924	.4996	.5068	.5142
250	.5216	.5291	.5367	.5443	.5520	.5598	.5677	.5757	.5833	.5919
260	.6002	.6085	.6169	.6254	.6339	.6427	.6514	.6602	.6691	.6781
270	.6872	.6964	.7057	.7151	.7246	.7341	.7437	.7534	.7633	.7732
280	.7832	.7933	.8036	.8139	.8242	.8348	.8454	.8561	.8668	.8778
290	.8887	.8998	.9110	.9223	.9337	.9452	.9568	.9686	.9803	.9922
300	1.0042	1.0163	1.0286	1.0409	1.0533	1.0659	1.0786	1.0913	1.1042	1.1171
310	1.1302	1.1433	1.1568	1.1702	1.1837	1.1973	1.2111	1.2250	1.2389	1.2531
320	1.2672	1.2816	1.2959	1.3105	1.3252	1.3400	1.3549	1.3699	1.3851	1.4003
330	1.4157	1.4312	1.4468	1.4626	1.4784	1.4944	1.5105	1.5267	1.5430	1.5595
340	1.5761	1.5928	1.6096	1.6267	1.6437	1.6609	1.6783	1.6958	1.7134	1.7311
350	1.7491	1.7670	1.7851	1.8033	1.8217	1.8402	1.8589	1.8777	1.8966	1.9157
360	1.9349	1.9541	1.9736	1.9932	2.0128	2.0326	2.0527	2.0728	2.0931	2.1135
370	2.1340	2.1547	2.1755	2.1965	2.2176	2.2388	2.2601	2.2817	2.3033	2.3251
380	2.3471	2.3691	2.3914	2.4138	2.4363	2.4589	2.4817	2.5046	2.5278	2.5511
390	2.5744	2.5980	2.6216	2.6456	2.6695	2.6936	2.7178	2.7423	2.7669	2.7916
400	2.8165	2.8415	2.8668	2.8921	2.9176	2.9432	2.9690	2.9949	3.0211	3.0473

[1] Standard gravity = 32.174 ft./sec.[2]

TABLE 5.—*Derivative of the pressure of saturated water vapor* ($dP/d\theta$)—Continued

Temperature θ	0	1	2	3	4	5	6	7	8	9
	Derivative									
°F.	*Lbs./in.²* / °F.	*Lbs./in.²* / °F.	*Lbs./in.²* / °F.	*Lbs./in.²* / °F.	*Lbs./in.²* / °F.	*Lbs./in.²* / °F.	*Lbs./in.²* / °F.	*Lbs./in.²* / °F.	*Lbs./in.²* / °F.	*Lbs./in.²* / °F.
410	3.0737	3.1004	3.1271	3.1540	3.1810	3.2082	3.2355	3.2631	3.2908	3.3186
420	3.3466	3.3747	3.4031	3.4316	3.4603	3.4891	3.5180	3.5472	3.5764	3.6060
430	3.6355	3.6654	3.6953	3.7254	3.7557	3.7862	3.8168	3.8475	3.8786	3.9097
440	3.9410	3.9724	4.0041	4.0358	4.0678	4.0999	4.1322	4.1648	4.1974	4.2303
450	4.2633	4.2965	4.3298	4.3633	4.3969	4.4308	4.4649	4.4992	4.5336	4.5681
460	4.6030	4.6379	4.6730	4.7083	4.7437	4.7794	4.8152	4.8513	4.8874	4.9238
470	4.9604	4.9971	5.034	5.071	5.108	5.146	5.184	5.221	5.259	5.298
480	5.336	5.375	5.413	5.453	5.492	5.531	5.571	5.610	5.650	5.691
490	5.731	5.771	5.812	5.853	5.894	5.935	5.977	6.018	6.060	6.102
500	6.144	6.187	6.230	6.273	6.316	6.359	6.402	6.446	6.489	6.534
510	6.578	6.622	6.667	6.712	6.757	6.803	6.848	6.894	6.939	6.986
520	7.032	7.079	7.126	7.172	7.219	7.267	7.315	7.363	7.411	7.458
530	7.506	7.554	7.602	7.651	7.700	7.750	7.800	7.850	7.900	7.951
540	8.002	8.053	8.104	8.155	8.207	8.259	8.312	8.364	8.416	8.469
550	8.522	8.575	8.629	8.683	8.737	8.791	8.846	8.901	8.956	9.011
560	9.067	9.123	9.179	9.236	9.292	9.349	9.407	9.464	9.521	9.579
570	9.637	9.695	9.754	9.813	9.872	9.932	9.992	10.052	10.112	10.172
580	10.233	10.294	10.355	10.417	10.479	10.541	10.604	10.667	10.730	10.793
590	10.856	10.920	10.984	11.049	11.114	11.179	11.244	11.310	11.376	11.442
600	11.508	11.575	11.642	11.710	11.778	11.846	11.914	11.982	12.051	12.120
610	12.190	12.260	12.330	12.401	12.472	12.543	12.614	12.686	12.758	12.830
620	12.903	12.976	13.050	13.124	13.198	13.273	13.348	13.424	13.500	13.576
630	13.652	13.729	13.806	13.884	13.962	14.041	14.120	14.199	14.278	14.358
640	14.439	14.520	14.602	14.684	14.766	14.849	14.933	15.017	15.102	15.187
650	15.272	15.357	15.444	15.531	15.619	15.707	15.796	15.886	15.976	16.066
660	16.157	16.249	16.342	16.435	16.529	16.624	16.719	16.815	16.912	17.010
670	17.109	17.208	17.308	17.409	17.511	17.613	17.717	17.822	17.928	18.034
680	18.142	18.251	18.361	18.471	18.582	18.696	18.810	18.925	19.042	19.159
690	19.280	19.401	19.522	19.646	19.771	19.898	20.025	20.155	20.286	20.419
700	20.553	20.690	20.828	20.968	21.111	21.254				

Tables 6 and 7 are reciprocal to Tables 3 and 4 and express the same relation of vapor pressure to temperature arranged to indicate temperatures corresponding to integral values of saturation pressures.

TABLE 6.—*Pressure of saturated water vapor*

[Even pressures in pounds [1] per square inch with corresponding temperatures in degrees Fahrenheit]

Pressure P	Temp. θ	Pressure P	Temp. θ	Pressure P	Temp. θ	Pressure P	Temp. θ
Lbs./in.²	°F.	*Lbs./in.²*	°F.	*Lbs./in.²*	°F.	*Lbs./in.²*	°F.
15	213.034	30	250.340	45	274.444	60	292.711
16	216.321	31	252.224	46	275.806	61	293.792
17	219.436	32	254.056	47	277.143	62	294.859
18	222.405	33	255.841	48	278.456	63	295.911
19	225.247	34	257.584	49	279.747	64	296.953
20	227.963	35	259.288	50	281.018	65	297.980
21	230.572	36	260.954	51	282.268	66	298.994
22	233.076	37	262.580	52	283.499	67	299.994
23	235.493	38	264.170	53	284.708	68	300.985
24	237.826	39	265.728	54	285.902	69	301.963
25	240.075	40	267.251	55	287.078	70	302.929
26	242.253	41	268.746	56	288.238	71	303.886
27	244.367	42	270.214	57	289.381	72	304.830
28	246.415	43	271.650	58	290.505	73	305.767
29	248.405	44	273.060	59	291.616	74	306.692

[1] Standard gravity = 32.174 ft./sec.²

TABLE 6.—*Pressure of saturated water vapor*—Continued

Pressure P	Temp. θ	Pressure P	Temp. θ	Pressure P	Temp. θ	Pressure P	Temp. θ
Lbs./in.²	°F.	*Lbs./in.²*	°F.	*Lbs./in.²*	°F.	*Lbs./in.²*	°F.
75	307.607	180	373.067	475	461.749	1,200	567.211
76	308.509	182	373.973	480	462.817	1,220	569.309
77	309.405	184	374.872	485	463.875	1,240	571.381
78	310.293	186	375.763	490	464.927	1,260	573.428
79	311.170	188	376.647	495	565.969	1,280	575.449
80	312.037	190	377.522	500	467.004	1,300	577.444
81	312.898	192	378.390	510	469.049	1,320	579.414
82	313.749	194	379.253	520	471.064	1,340	581.362
83	314.595	196	380.110	530	473.049	1,360	583.290
84	315.429	198	380.958	540	475.008	1,380	585.197
85	316.255	200	381.799	550	476.939	1,400	587.082
86	317.074	205	383.868	560	478.841	1,420	588.946
87	317.886	210	385.903	570	480.717	1,440	590.789
88	318.691	215	387.905	580	482.566	1,460	592.615
89	319.488	220	389.868	590	484.395	1,480	594.421
90	320.279	225	391.794	600	486.201	1,500	596.208
91	321.061	230	393.687	610	487.983	1,520	597.972
92	321.838	235	395.549	620	489.742	1,540	599.718
93	322.607	240	397.382	630	491.479	1,560	601.446
94	323.370	245	399.186	640	493.195	1,580	603.162
95	324.129	250	400.961	650	494.892	1,600	604.863
96	324.879	255	402.708	660	496.568	1,620	606.546
97	325.623	260	404.428	670	498.224	1,640	608.215
98	326.361	265	406.123	680	499.863	1,660	609.866
99	327.093	270	407.793	690	501.482	1,680	611.499
100	327.819	275	409.439	700	503.086	1,700	613.114
102	329.257	280	411.061	710	504.671	1,720	614.716
104	330.671	285	412.662	720	506.239	1,740	616.307
106	332.062	290	414.240	730	507.790	1,760	617.885
108	333.434	295	415.799	740	509.324	1,780	619.450
110	334.786	300	417.337	750	510.844	1,800	621.000
112	336.118	305	418.855	760	512.349	1,820	622.529
114	337.431	310	420.354	770	513.837	1,840	624.047
116	338.725	315	421.835	780	515.313	1,860	625.556
118	340.002	320	423.297	790	516.772	1,880	627.052
120	341.263	325	424.742	800	518.216	1,900	628.535
122	342.507	330	426.170	810	519.650	1,920	630,007
124	343.734	335	427.580	820	521.068	1,940	631.468
126	344.946	340	428.975	830	522.474	1,960	632.918
128	346.143	345	430.357	840	523.867	1,980	634.351
130	347.326	350	431.721	850	525.248	2,000	635.773
132	348.495	355	433.070	860	526.614	2,050	639.286
134	349.649	360	434.404	870	527.969	2,100	642.730
136	350.790	365	435.722	880	529.313	2,150	646.108
138	351.917	370	437.026	890	530.649	2,200	649.423
140	353.033	375	438.319	900	531.970	2,250	652.678
142	354.137	380	439.599	910	533.281	2,300	655.873
144	355.228	385	440.866	920	534.579	2,350	659.013
146	356.304	390	442.120	930	565.857	2,400	662.098
148	357.370	395	443.362	940	537.144	2,450	665.132
150	358.426	400	444.590	950	538.412	2,500	668.112
152	359.469	405	445.808	960	539.670	2,550	671.041
154	360.504	410	447.014	970	540.917	2,600	673.922
156	361.528	415	448.209	980	542.155	2,650	676.755
158	362.542	420	449.394	990	543.383	2,700	679.542
160	363.545	425	450.566	1,000	544.600	2,750	682.283
162	364.538	430	451.729	1,020	547.012	2,800	684.981
164	365.521	435	452.881	1,040	549.386	2,850	687.632
166	366.496	440	454.023	1,060	551.726	2,900	690.241
168	367.462	445	455.153	1,080	554.033	2,950	692.810
170	368.417	450	456.275	1,100	556.305	3,000	695.336
172	369.364	455	457.388	1,120	558.544	3,050	697.822
174	370.303	460	458.493	1,140	560.753	3,100	700.272
176	371.232	465	459.588	1,160	562.935	3,150	702.679
178	372.153	470	460.674	1,180	565.086	3,200	705.052

TABLE 7.—*Pressure of saturated water vapor*

[Even pressures in kilograms[1] per square centimeter with corresponding temperatures in degrees centigrade]

Pressure P	Temperature θ	Pressure P	Temperature θ	Pressure P	Temperature θ	Pressure P	Temperature θ
Kg/cm²	*°C.*	*Kg/cm²*	*°C.*	*Kg/cm²*	*°C.*	*Kg/cm²*	*°C.*
1.0	99.072	8.0	169.605	55	268.693	120	323.148
1.1	101.764	8.2	170.626	56	269.842	122	324.408
1.2	104.246	8.4	171.629	57	270.974	124	325.654
1.3	106.565	8.6	172.613	58	272.092	126	326.884
1.4	108.739	8.8	173.579	59	273.195	128	328.098
1.5	110.789	9.0	174.526	60	274.285	130	329.298
1.6	112.730	9.2	175.458	61	275.361	132	330.484
1.7	114.575	9.4	176.375	62	276.423	134	331.657
1.8	116.331	9.6	177.276	63	277.472	136	332.816
1.9	118.010	9.8	178.163	64	278.509	138	333.958
2.0	119.617	10	179.035	65	279.534	140	335.088
2.1	121.161	11	183.201	66	280.547	142	336.206
2.2	122.646	12	187.079	67	281.548	144	337.312
2.3	124.076	13	190.708	68	282.537	146	338.406
2.4	125.457	14	194.130	69	283.517	148	339.488
2.5	126.790	15	197.360	70	284.485	150	340.559
2.6	128.083	16	200.429	71	285.441	152	341.616
2.7	129.335	17	203.351	72	286.388	154	342.661
2.8	130.549	18	206.145	73	287.326	156	343.696
2.9	131.730	19	208.819	74	288.252	158	344.722
3.0	132.878	20	211.385	75	289.170	160	345.737
3.1	133.994	21	213.855	76	290.079	162	346.742
3.2	135.082	22	216.234	77	290.978	164	347.738
3.3	136.143	23	218.530	78	291.867	166	348.723
3.4	137.178	24	220.753	79	292.748	168	349.699
3.5	138.188	25	222.905	80	293.621	170	350.664
3.6	139.178	26	224.988	81	294.486	172	351.620
3.7	140.144	27	227.012	82	295.343	174	352.565
3.8	141.089	28	228.979	83	296.191	176	353.502
3.9	142.015	29	230.894	84	297.032	178	354.432
4.0	142.922	30	232.757	85	297.865	180	355.353
4.1	143.810	31	234.572	86	298.690	182	356.263
4.2	144.680	32	236.345	87	299.508	184	357.165
4.3	145.534	33	238.075	88	300.319	186	358.058
4.4	146.374	34	239.766	89	301.123	188	358.943
4.5	147.200	35	241.419	90	301.919	190	359.821
4.6	148.008	36	243.035	91	302.710	192	360.689
4.7	148.802	37	244.617	92	303.493	194	361.551
4.8	149.584	38	246.167	93	304.270	196	362.404
4.9	150.354	39	247.687	94	305.041	198	363.248
5.0	151.110	40	249.176	95	305.804	200	364.084
5.2	152.586	41	250.637	96	306.562	202	364.913
5.4	154.018	42	252.073	97	307.314	204	365.734
5.6	155.409	43	253.483	98	308.060	206	366.550
5.8	156.760	44	254.866	99	308.799	208	367.358
6.0	158.075	45	256.224	100	309.533	210	368.157
6.2	159.354	46	257.562	102	310.986	212	368.949
6.4	160.602	47	258.876	104	312.418	214	369.734
6.6	161.820	48	260.171	106	313.828	216	370.511
6.8	163.008	49	261.443	108	315.214	218	371.280
7.0	164.168	50	262.697	110	316.580	220	372.042
7.2	165.303	51	263.931	112	317.930	222	372.800
7.4	166.412	52	265.149	114	319.264	224	373.553
7.6	167.497	53	266.347	116	320.577	225	373.926
7.8	168.563	54	267.527	118	321.871		

[1] Standard gravity=980.665 cm/sec.²

VI. ESTIMATION OF ACCURACY

Numerical values of physical quantities derived from measurements are never in exact accord with the true values. No matter how skillful and diligent the experimenter, there is a limit to the precision attained in each separate element of measurement and in the final result. The practical use of physical data is similarly subject to limitations of accuracy. The compiler of tables of properties of steam for practical use is obliged to choose from available experimental sources the definitive values which are to be used as a basis for formulation. This selection may be aided by the experimenter if in addition to the record of methods, standards, and units used in his measurements, he includes also a judicious appraisal of the accuracy of the results.

By careful study of all the factors which enter into the measurements, an estimate may be made of the magnitude of the systematic error which may still remain in each factor after all known corrections for standards and calibrations have been applied. Having made these preliminary estimates, they may be used in a final estimate of the amount by which the results of the measurements might differ from the truth. Such an analysis has been made for the results of the present investigation by considering every apparent source of error, both systematic and accidental.

The sources of systematic error which have been found significant, include the calibration of the piston gage, the determination of the pressure corrections for the connecting line between the water sample and the gage, the difference of the scale of the thermometer used from the ideal international standard temperature scale, and the determination of the actual temperature of the free surface of the water sample relative to the thermometer. Each of these factors has been discussed earlier in its proper place. The magnitude of the accidental errors of measurement was deduced from the actual differences in the individual results.

Obviously, the final appraisal of accuracy can be only approximate. If the facts were known on which an exact estimate of the systematic errors could be based, corrections could be applied for them and their effect eliminated. The element of judgment must enter in the figure which is deduced to indicate the uncertainty remaining after all known corrections have been applied. As such an approximate appraisal, it is believed that the values formulated for the pressure of saturated water vapor do not differ from the truth by more than 3 parts in 10,000, with the possible exception of the region near the critical, where the rapidly changing properties of water make the measurements somewhat less trustworthy.

VII. ACKNOWLEDGMENT

The work presented in this report marks a further step in the effort to establish reliability and accord in steam tables, a project which has been promoted by the American Society of Mechanical Engineers through the material support of the steam power industries. It is hoped that the results here given may prove an aid in attaining that object.

WASHINGTON, October 15, 1932.

RP524

SOME FUSION PROPERTIES OF GROUND COAT ENAMELS AS INFLUENCED BY COMPOSITION

By W. N. Harrison and B. J. Sweo

ABSTRACT

The compositions of nine vitreous ground coat enamels for sheet iron were varied within a region approximating commercial practice by substituting silica (added as flint) for feldspar, and by substituting boric oxide for sodium oxide, and vice versa. In two other enamels the above named fluxes were varied as a unit against the refractories as a unit. The fusion properties of the enamels were studied through determinations of (1) temperature of maximum heat absorption, (2) softening temperature as observed with the interferometer, (3) cone deformation temperature, (4) "button" deformation behavior, and (5) fusion block deformation behavior. The conclusions were: (*a*) Increasing silica at the expense of feldspar increased the refractoriness moderately and approximately uniformly. (*b*) Increasing boric oxide at the expense of sodium oxide caused an increase in refractoriness which varied with the percentages of these constituents. It was quite marked when the boric oxide content was near its minimum and the sodium oxide content near its maximum, but diminished progressively as the opposite limits of composition were approached. (*c*) The extent of this variation was different for different tests, and diminished as the amount of flow required to complete the respective tests increased. This effect was probably due to the fact that differences in viscosity of the enamels had more opportunity to influence the results of those tests which involved a greater flow of the specimens. (*d*) The mean end temperatures of the various tests increased as the amount of flow required to complete the tests increased. (*e*) More systematic comparisons of enamels could be made by measuring the heat treatment necessary to produce a given effect than by submitting all samples to the same treatment and distinguishing between them by the varying effect produced. (*f*) Application of the enamels to test pieces under varying conditions indicated that all of the tests placed them in approximately the correct order of fusibility.

CONTENTS

	Page
I. Introduction	190
II. Compositions of enamels studied	190
III. Preparation of enamels	192
IV. Description of tests and analysis of results	193
1. Temperatures of maximum heat absorption	193
(*a*) Description of test	194
(*b*) Location of end point	195
(*c*) Analysis of results	195
2. Initial deformation temperatures by interferometer method	197
3. Cone deformation temperatures	198
(*a*) Description of test	198
(*b*) Analysis of results	199
4. Button tests	200
(*a*) Variable end point principle	201
(*b*) Constant end point principle	202
5. Fusion block tests	203
V. Correlation of fusion tests with each other and with firing behavior of the enamels	205
VI. Summary and conclusions	208

I. INTRODUCTION

The general subject of the relation between composition and properties is a familiar one to enamel technologists. The broad purpose of investigations in this field is to enable the enameler to predict the important properties of an enamel from its composition, or conversely to estimate with sufficient accuracy the composition which will be required to produce an enamel of given properties lying within attainable limits.

While substantial progress has been made in the investigation of this general subject, still greater steps remain to be taken. The magnitude of the task is better appreciated when it is borne in mind that results in the literature taken as a whole give no assurance that relations exist which hold good without modification for enamels, glazes, and glasses alike, nor indeed for wide variations in composition within these classes.[1] Hence to secure results of the greatest practical usefulness it is desirable to work with specimens representing a range of compositions which are typical of actual commercial practice and which extend beyond such limits only for special reasons.

In accordance with this conception the investigation reported here concerns a group of enamels with a restricted range of compositions embracing typical commercial ground coats for sheet iron. Further, it concerns in the main only one type of the characteristics of these enamels, namely, fusion behavior.[2] This report forms the first in a series, of which later units will deal with other specific properties of the same enamels.

II. COMPOSITIONS OF ENAMELS STUDIED

The plan was to vary the compositions in such manner and proportions as would be fairly typical of commercial practice.[3] No attempt was made to include the extreme limits of compositions which have been used commercially, nor to include all ingredients which have been successfully used in commercial ground-coat enamels. The scheme of variations in composition is given in Table 1, which also includes the results of various tests discussed later in this paper. The first nine enamels (A to I, inclusive) all contained 30 per cent sodium oxide plus boric oxide, 60 per cent silica (added as flint) plus feldspar, and 10 per cent fluorspar plus the oxides of manganese and cobalt. The percentages of the ingredients constituting the 10 per cent portion were kept constant throughout the series, substitutions being made only between sodium and boric oxides and between flint and feldspar. Feldspar, although it contains more than two elements, was varied as a unit in this investigation because that is the usual commercial practice. Enamels J and K do not fit into the system of variation governing the first nine compositions, but are

[1] In this connection special attention is called to International Critical Tables, vol. 2 pp. 87 to 106 (first edition), and to the work of F. P. Hall, "The Influence of Chemical Composition on the Physical Properties of Glazes"; J. Am. Cer. Soc., vol. 13, no. 3, p. 182, March, 1930.

[2] Although the use of the word "melt" to describe the action of enamels and similar materials when subjected to high temperatures may be of questionable accuracy, the use of "fuse" would seem entirely proper if only for its secondary meaning of "unite" or "coalesce," which would apply to the action of the enamel grains when the material is powdered before heating, as it is in the application of enamels to metal. All tests reported in this paper except those made with the interferometer were performed on samples which had been powdered prior to testing.

[3] Use was made of an opinion obtained from R. R. Danielson as to the most prevalent commercial practice in this respect.

included in order to study the effect of altering the described scheme of variation by raising the content of silica and feldspar simultaneously at the expense of both sodium and boric oxides, and conversely of raising the total of the latter two at the expense of the former.

TABLE 1.—*Scheme of variation in composition, and results of tests* [1]

Enamel designation	Variable constituents [2]				Temperature of maximum heat absorption [3]		Softening temperature by interferometer method [4]		Cone deformation temperature [5]		"Button-test" end temperature [6]		Fusion block test			
													"Start" temperature [3]		"Finish" temperature [3]	
	Feldspar	Flint	Sodium oxide	Boric oxide												
	Per cent	*Per cent*	*Per cent*	*Per cent*	*° C.*	*° F.*	*° C.*	*° F.*	*° C.*	*° F.*	*° C.*	*° F.*	*° C.*	*° F.*	*° C.*	*° F.*
A	35	25	17	13	488	910	513	955	644	1,191	697	1,287	705	1,301	737	1,359
B	35	25	14	16	520	968	550	1,022	675	1,247	726	1,339	733	1,351	770	1,458
C	35	25	11	19	531	988	558	1,037	693	1,279	750	1,382	757	1,395	799	1,470
D	30	30	17	13	493	919	518	964	654	1,209	705	1,301	706	1,303	742	1,368
E	30	30	14	16	525	977	555	1,031	680	1,256	734	1,353	735	1,355	776	1,429
F	30	30	11	19	536	997	562	1,044	701	1,294	759	1,398	761	1,402	805	1,481
G	25	35	17	13	499	930	522	971	661	1,222	712	1,314	717	1,323	752	1,386
H	25	35	14	16	531	988	560	1,040	685	1,265	742	1,368	750	1,382	785	1,445
I	25	35	11	19	542	1,008	569	1,056	705	1,301	765	1,409	775	1,427	814	1,497
J	27	27	17	19	501	934	521	969	641	1,186	706	1,303	709	1,308	740	1,364
K	33	33	11	13	540	1,004	565	1,049	722	1,332	771	1,420	784	1,443	827	1,521

[1] The temperatures in this table are reported to 1°, not because the absolute values are necessarily correct within 1°, but because the differences in temperature with variations in composition can be more accurately determined from exact than from rounded figures, in view of the fact that each reported value is based on from 3 to 24 determinations.

[2] Each enamel contained, in addition to the above constituents, 7.7 per cent of fluorspar, 1.7 per cent of manganese oxide, and 0.6 per cent of cobalt oxide.

[3] Means of 6 values from duplicate determinations on each of 3 samples.

[4] Means of 3 determinations on 3 different samples.

[5] Means of 24 determinations, 8 on each of 3 batches.

[6] Each value based on 6 to 9 determinations.

The compositions of the batches were calculated from the results of chemical analyses of the raw materials, and are given in Table 2. The calculated melted compositions are given in Table 3, together with the results of analyses of the enamel frits.

TABLE 2.—*Compositions of raw batches calculated to give 100 parts of enamel*

Enamel designation	Ingredients (parts by weight)								
	Borax	Feldspar	Quartz	Soda ash	Soda niter	Fluorspar	Cobalt oxide	Manganese oxide	Total
A	34.90	35.38	24.75	16.53	5.00	8.06	0.60	1.94	127.16
B	43.00	35.38	24.75	8.92	5.00	8.06	.60	1.94	127.65
C	51.00	35.38	24.75	1.30	5.00	8.06	.60	1.94	128.03
D	34.90	30.30	29.76	16.53	5.00	8.06	.60	1.94	127.09
E	43.00	30.30	29.76	8.92	5.00	8.06	.60	1.94	127.58
F	51.00	30.30	29.76	1.30	5.00	8.06	.60	1.94	127.96
G	34.90	25.26	34.76	16.53	5.00	8.06	.60	1.94	127.05
H	43.00	25.26	34.76	8.92	5.00	8.06	.60	1.94	127.54
I	51.00	25.26	34.76	1.30	5.00	8.06	.60	1.94	127.92
J	51.00	27.28	26.75	11.83	5.00	8.06	.60	1.94	132.46
K	34.90	33.35	32.76	6.00	5.00	8.06	.60	1.94	127.11

TABLE 3.—*Chemical compositions of finished enamels, as calculated from Table 2, and as indicated by the results of chemical alalysis* [1]

Enamel	Constituents [2]						
	B_2O_3	Na_2O	K_2O	SiO_2	Al_2O_3	Ca	F_2
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
A	13.0	17.7	4.4	48.6	6.4	4.0	3.7
	13.1	*16.9*	*4.5*	*48.2*	*6.8*	*4.1*	*3.4*
B	16.0	14.7	4.4	48.6	6.4	4.0	3.7
	16.9	*14.2*	*4.6*	*50.3*	*6.7*	*4.1*	*3.1*
C	19.0	11.7	4.4	48.6	6.4	4.0	3.7
	18.8	*11.1*	*4.4*	*49.8*	*6.8*	*4.1*	*3.1*
D	13.0	17.6	3.8	50.3	5.5	4.0	3.7
	13.1	*17.0*	*3.9*	*50.9*	*5.8*	*4.0*	*3.2*
E	16.0	14.6	3.8	50.3	5.5	4.0	3.7
	16.3	*14.0*	*3.9*	*51.1*	*5.7*	*4.0*	*3.1*
F	19.0	11.6	3.8	50.3	5.5	4.0	3.7
	19.0	*11.1*	*3.8*	*50.6*	*6.1*	*4.0*	*3.0*
G	13.0	17.5	3.1	51.9	4.6	4.0	3.7
	13.3	*16.7*	*3.3*	*51.8*	*4.9*	*4.1*	*3.1*
H	16.0	14.5	3.1	51.9	4.6	4.0	3.7
	16.6	*13.8*	*3.3*	*51.8*	*5.0*	*4.1*	*2.8*
I	19.0	11.5	3.1	51.9	4.6	4.0	3.7
	19.3	*10.9*	*3.2*	*51.9*	*5.0*	*4.1*	*2.9*
J	19.0	17.6	3.4	45.3	4.9	4.0	3.7
	19.4	*16.7*	*3.6*	*45.0*	*5.3*	*4.0*	*3.1*
K	13.0	11.7	4.1	55.3	6.0	4.0	3.7
	13.2	*11.4*	*4.3*	*55.3*	*6.5*	*4.0*	*3.0*

[1] Values in roman type were calculated, and those in italics were obtained by chemical analysis. The analyses were made by J. F. Klekotka and F. W. Glaze, of the Bureau of Standards.

[2] Only a part of the enamels were analyzed for cobalt and manganese oxides, but the indication was that all may be considered as having the theoretical content of 0.6 per cent cobalt, reported as Co_3O_4, and 1.7 per cent of manganese oxide reported as MnO_2. The values reported from analytical results are averages from analysis of two of the triplicate batches, except for enamels G and H, and all fluorine values, each of which is based on analysis of only one enamel batch.

III. PREPARATION OF ENAMELS

Each individual raw material was thoroughly mixed in a pebble mill and placed in sealed containers to prevent contamination or change in moisture content before use. The batches were made up in quantities sufficient to give 1 kg, melted weight, of each enamel. A second set of batches was made to duplicate the first. Each of these raw batches was divided into halves. Three of the four resulting lots were used, and were smelted in 75 ml platinum crucibles to avoid contamination by partial solution of fire-clay crucibles. Each half batch made four such crucible batches, which were combined after smelting, so that finally each enamel was available for test in triplicate. The enamels were identified by the first 11 letters of the alphabet, and the triplicate batches distinguished numerically. Two of the three sets (one from each of the two original raw batches) were analyzed to obtain the results given in Table 3.

The furnace used for smelting was similar to one described by F. H. Norton and C. L. Norton, jr.[4]

The heating arrangement was modified to permit better temperature control and to insure oxidizing conditions. This change was effected by using a burner which, although of essentially the same type, had

[4] Norton, F. H., and Norton, C. L., jr., A Small, Gas-fired Laboratory Furnace, J. Am. Cer. Soc., vol. 13 (3), p. 161, 1930.

additional facilities for a forced air supply. Both gas pressure and air pressure were controlled, and the temperatures could be held constant within about ± 5° C. (9° F.). The enamels were all smelted at approximately 1,250° C. (2,280° F.) for one hour and stirred during smelting at 10-minute intervals with a small nickel rod. After smelting they were fritted in cold water, dried, and pulverized in a mortar to pass a No. 150 sieve.

IV. DESCRIPTION OF TESTS AND ANALYSIS OF RESULTS

Various methods of testing the fusibility or refractoriness of enamels are in use. To what extent the results obtained by these methods may be correlated, and whether or not it is practicable to convert values expressed in terms of one test into equivalent values in terms of another, are among the questions which it is hoped the present study will clarify. Further, the various tests on fusibility were carried out with the object of investigating the effect of the specified variations in composition upon the fusion behavior of the enamels. Stated briefly, the dual object was to compare the tests and to compare the enamels.

1. TEMPERATURES OF MAXIMUM HEAT ABSORPTION

Determinations of the temperatures of maximum rate of heat absorption were included because there is evidence to support the view that an enamel when heated to a sufficiently high temperature undergoes a readjustment, as indicated by the absorption of heat. Above this temperature the material deforms at a rate which increases with the temperature. Such a conception ranks the temperature of maximum heat absorption as a closer approximation to a true "fusion" temperature than any of the other tests described in this paper. Thus these determinations supply something which at least approaches a constant of the material, and with which the other tests, more adaptable to shop and industrial laboratory use, may be compared. They may serve a further useful purpose in certain fields of composition by virtue of their close reproducibility because, on comparison of enamels intended to have the same composition, any considerable difference in the temperatures of maximum heat absorption indicates a departure from the desired composition. Another reason why these determinations are desirable is because they indicate an annealing temperature of the enamels, falling as they do about midway in the annealing range. Thus the readjustment takes place within a range of temperature between the lower and upper critical temperatures; that is, between the temperature at which the rate of thermal dilatation per degree rise in temperature suddenly increases, and the temperature at which vertical elongation becomes negative due to softening of the specimen.[5]

The exact temperature at which the rate of readjustment, and hence the rate of heat absorption, is most rapid depends to some extent on the thermal history of the specimen and the rate of increase of temperature during the test. Closely reproducible results may be obtained, however, if the specimens are heated before testing to a

[5] Tool and Valasek, B. S. Sci. Paper No. 358, 1920; Tool and Eichlin, B. S. Jour. Research, Vol. 6 (RP292), p. 523, April, 1931; Peters and Cragoe, B. S. Sci. Paper No. 393, 1920.

temperature at which all strains are relieved, cooled at a suitable rate, and then tested at a reasonably constant rate of temperature elevation.[6]

(a) DESCRIPTION OF TEST

The test was made as follows: A 20 g portion of the powdered enamel was placed in a 25 ml platinum crucible, which was then placed approximately in the center of an electric muffle furnace having inside dimensions of 7 by 5 by 12 inches. The junction of a platinum, platinum-rhodium thermocouple was placed near the center of the sample. The cold junction of the thermocouple was kept at 0° C., and the emf was indicated by means of a type K potentiometer graduated to 0.0005 mv. The temperature of the

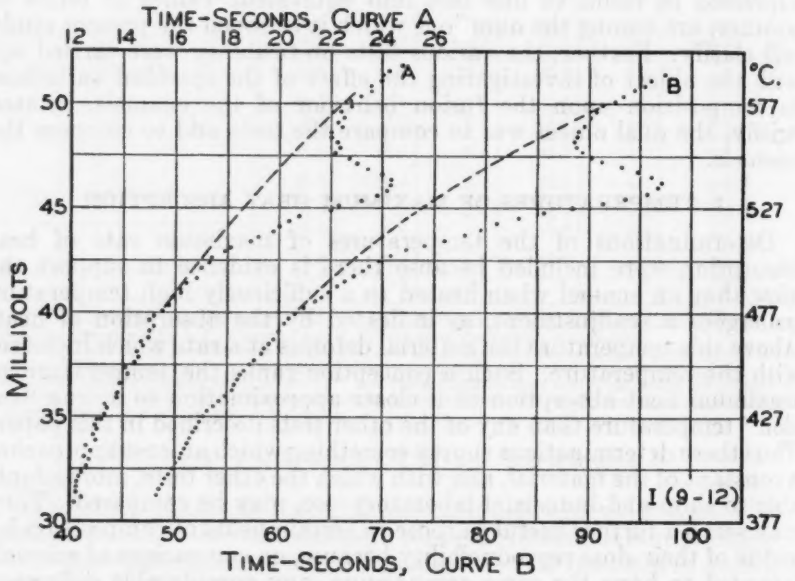


FIGURE 1.—*Typical inverse rate heating curve (enamel I, specimen 9–12) as used to determine temperature of maximum rate of heat absorption*

Curve *A* shows time interval (upper scale) required for 2.5° C. increase in temperature at the average temperature (emf) indicated by each point on curve. Curve *B* shows time interval (lower scale) required for 10.0° C. increase in temperature at the average temperature (emf) indicated by each point on curve.

sample was then raised to approximately 75° C. above its initial deformation temperature as determined with the interferometer and allowed to cool in the furnace, thus preparing it for the test. This treatment incidentally caused a sintering effect in the powdered enamel, and firmly fixed the thermocouple in place. The temperature of the sample was increased at a rate of 5° to 6° C. per minute in the temperature range of maximum heat absorption. A typical temperature schedule is shown in the inverse rate curves in Figure 1.[7] From curve *B* it may be seen that the rate of temperature increase just before the heat absorption began (about 470° C.) was approximately 10° C. per minute, and at the end of the test was a little over

[6] See second item, footnote 5.

[7] See first item, footnote 5.

6° C. per minute. The dotted line indicates approximately the temperature schedule of the furnace itself between these temperatures.

After one set of observations had been completed, the sample was prepared for a second test by allowing the elevation in temperature to continue until it again reached 75° C. above the initial deformation temperature, so that its condition due to thermal history would be virtually the same as before the test. After cooling, a second determination was made on each sample.

(b) LOCATION OF END POINT

Curve *A*, in Figure 1, was plotted from the data as obtained. Exactly the same data were used to compute the points in curve *B*, and each point on the latter represents the sum of four points on the former. For example, the time-increment value of the bottom point of curve *B* is obtained by adding the time-increment values of the first four points of the original data (curve *A*). The next higher point is obtained from the second, third, fourth, and fifth original points, etc. By the use of this system a more accurate location of the point of maximum deflection could be accomplished, and better agreement between check determinations was obtained because mechanical and personal errors were largely compensated.

The point of maximum deflection was estimated from the computed curves to 0.005 mv (0.5° C.), and at least two determinations were made on each sample. The average deviation of the individual values from the mean of the two determinations was 0.6° C. (1.1° F.) and the maximum deviation was 1.5° C. (2.7° F.). The values obtained by the two determinations on a given sample were averaged with the corresponding values for the other two of the triplicate samples, and the final averages are given in Table 1. The average individual deviation from mean in this case was 0.9° C. (1.6° F.) and the maximum 2.3° C. (4.1° F.).

(c) ANALYSIS OF RESULTS

From the data in Table 1 it may be seen that the increase of silica from 25 to 30 per cent at the expense of feldspar caused an increase in the temperature of maximum heat absorption of 5° C. (9° F.). This conclusion is based upon the results of 36 determinations, since it involves six mean values (for enamels A, B, C, D, E, and F, respectively) each of which is obtained from six determinations. In a similar manner, the conclusion that the further increase of silica to 35 per cent at the expense of feldspar caused a 6° C. (11° F.) increase is also based upon 36 determinations. Disregarding the slight difference in magnitude of effect between the first and second substitutions, it may be stated that in every case the temperature of maximum heat absorption increased approximately 1.1° C. (2° F.) for each substitution of 1 part of silica for 1 part of feldspar.

No such generalization is applicable in describing the effect of increasing boric oxide at the expense of sodium oxide while the percentages of silica and feldspar remained constant. Enamels A, B, and C all have 25 per cent feldspar and 35 per cent silica, and in the order named boric oxide is increased from 13 to 19 per cent at the expense of sodium oxide, which is reduced from 17 to 11 per cent. The substitution of 3 parts of boric oxide for 3 parts of sodium oxide, as indicated in enamels A and B, caused an elevation in the determined

temperature of 32° C. (58° F.), but the further substitution of 3 more parts of boric oxide for 3 parts of sodium oxide, as indicated in enamels B and C caused a further elevation of only 11° C. (20° F.), or about one-third as much.

The parallel case of enamels D, E, and F, in which silica and feldspar are both maintained at 30 per cent while sodium oxide and boric oxide are varied as in the preceding group, shows exactly the same relation which prevails also in the third parallel case, comprising enamels G, H, and I.

Here again, the general conclusion that the first 3 per cent increase in boric oxide at the expense of sodium oxide caused a 32° C. (58° F.) rise in the determined temperature, is based upon 36 determinations, and the statement that the second 3 per cent substitution

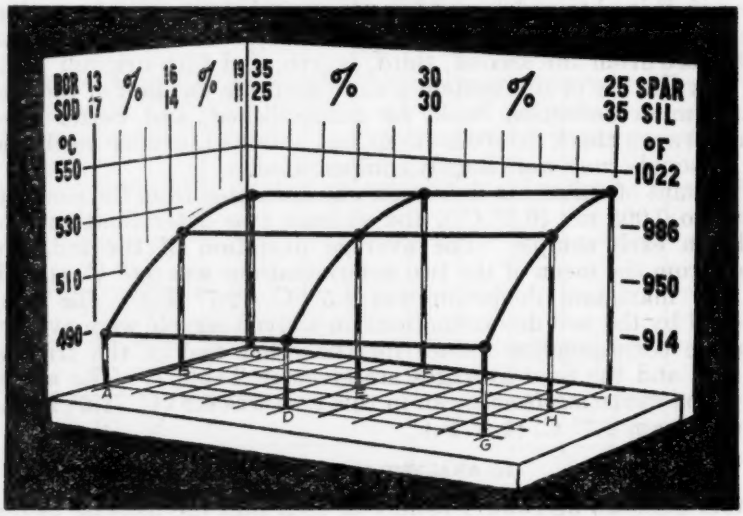


FIGURE 2.—*Variation in temperatures of maximum heat absorption with the compositions of the enamels*

Key: *SPAR*=Feldspar (considered as a unit).
SIL =Silica added as flint.
BOR =Boric oxide.
SOD =Sodium oxide.

causes an 11° C. (20° F.) rise is based upon a like number. The values for enamels J and K show that when boric and sodium oxides are decreased together from 19 and 17 per cent, respectively, to 13 and 11 per cent, respectively, with simultaneous increase of feldspar and silica from 27 per cent of each to 33 per cent of each, the temperature of maximum heat absorption is increased 39° C. (70° F.).

This system of relations may be visualized more readily with the aid of a suitable diagram. Accordingly a space model was constructed and projected in perspective as in Figure 2. In this figure silica increases at the expense of feldspar from left to right, and boric oxide increases at the expense of sodium oxide from front to rear. The letters at the base of the pillars designate the enamels having compositions corresponding to the positions of the pillars on the base

plane. These compositions are the ones given in Table 1, except that J and K are omitted. The vertical scale represents temperatures of maximum heat absorption. The base plane is arbitrarily set at the level of 470° C. (878° F.), and the determined value for any of the enamels can be closely approximated by adding to this temperature an amount determined by counting the alternate light and dark bands, or fraction thereof, on the pillar corresponding to the enamel in question. Each band has a length corresponding to a temperature interval of 10° C. (18° F.). Reference to these bands minimizes any error of parallax in reading the diagram.

This figure illustrates graphically the relations which were obtained from the data in Table 1. In addition, it has the advantage that it enables the observer to visualize simultaneously these several relations and their mutual interdependence. It is apparent from this figure that substituting silica for feldspar caused virtually a straight line increase in the temperature of maximum heat absorption and that this increase is the same for all three groups of enamels in which the percentages of boric and sodium oxide are fixed. It is also apparent that the substitution of boric oxide for sodium oxide caused an increase in the determined temperature which does not follow a straight line, inasmuch as the effect per unit of substitution decreases as the substitution progresses.

Although the compositions of enamels J and K are outside of the field shown in this diagram, the latter may be used with reference to these two enamels by comparing their determined temperatures as given in Table 1 with the observed points for other enamels which are given in the diagram. A comparison of this sort indicates that the high flux enamel J has about the same maximum heat absorption temperature as enamel G and the low flux enamel K has about the same maximum heat absorption temperature as enamel I. A comprehensive statement of this relation is as follows: The simultaneous decrease from 19 to 13 per cent B_2O_3, and from 17 to 11 per cent Na_2O, accompanied by a corresponding increase from 27 to 33 per cent each of silica and feldspar, caused approximately the same increase in the temperature of maximum heat absorption as was caused by increasing boric oxide from 13 to 19 per cent with a simultaneous reduction of sodium oxide from 17 to 11 per cent.

The immediately preceding statement could have been expressed more conveniently in an abbreviated form by saying that the J–K change caused about the same increase in the determined temperature as the G–I change. From this point on, this abbreviated form of expression will be used.

2. INITIAL DEFORMATION TEMPERATURES BY INTERFEROMETER METHOD [8]

The specimens used for the interferometer tests were segments of rods which had been drawn from the molten frit. They were about 3 mm in diameter and 5 mm in height. The bottom end of each specimen was ground to form three short legs, and the top to form a cone of gently sloping sides and a slightly blunted point. When these

[8] The interferometer, and method of using it, is described by G. E. Merritt, in B. S. Sci. Paper No. 485, 1924.

specimens were heated in the interferometer to temperatures approximating 25° C. (45° F.) above their respective temperatures of maximum heat absorption they softened sufficiently so that a slumping movement could be detected.[9] The temperature at which this deformation occurred is referred to here as the initial deformation temperature.[10] This temperature may vary somewhat with the heating rate, the weight of the upper quartz plate, and the shape of the specimens. All of these factors were therefore kept as constant as possible, the heating rate being 3° C. per minute.

The averages of three determinations on the three different batches of each of 11 enamels are given in Table 1 and bear quite a symmetrical relation one to another. The mean deviation from the average results reported was 3° C. (5.4° F.) and the maximum was 10° C. (18° F). A graphical arrangement (not shown) of these data bears a striking similarity to Figure 2. The outstanding differences are that this phenomenon occurred at approximately 25° C. (45° F.) higher temperature, and that in the relation between the substitution of boric for sodium oxide and the elevation in the determined temperature, the deviation from a straight line is even more pronounced than in the case of Figure 2. Thus the mean elevation in softening temperature caused by the A–B, D–E, and G–H changes in composition is 37° C. (67° F.) and the mean for the B–C, E–F, and H–I changes is 8° C. (14° F.). Each of these mean values (37° and 8° C.) is based upon the results of 18 determinations. The ratio of the smaller temperature increase to the larger is about two-ninths, which compares with about three-ninths in Figure 2.

By interpolation it was estimated that a 1 per cent substitution of boric oxide for sodium oxide beginning with composition A, D, or G would elevate the softening temperature approximately ten times as much as a similar 1 per cent substitution, ending with composition, C, F, or I. This ratio of 10 to 1 corresponds with that of 6 to 1 in the case of the temperatures of maximum heat absorption.

The mean elevation in softening temperature caused by the A–G, B–H, and C–I changes in composition was virtually the same as in Figure 2, being 10° C. (18° F.) as against 11° C. (20° F.). Thus it appears that the substitution of silica for feldspar, within the limits studied, causes approximately a straight line increase in the initial deformation temperature of 1° C. (1.8° F.) for each 1 per cent substitution.[11]

3. CONE DEFORMATION TEMPERATURES

(a) DESCRIPTION OF TEST

The cone deformation tests were modeled after the tentative standard method of the enamel division, American Ceramic Society.[12] Instead of the standard size cones, 2½ inches high, cones 1¼ inches high were used, because the supply of each enamel was limited. In order to minimize breakage in handling, the dried cones were slightly

[9] The data obtained in these tests relative to coefficient of expansion were reserved for a separate publication.

[10] Some authors have called this temperature the initial softening temperature.

[11] The results reported here were obtained on first heatings of the specimens involved. Second heatings, carried out in connection with expansivity determinations, gave results generally a few degrees higher, but bearing the same relationship to one another.

[12] Bull. Am. Cer. Soc., p. 269, September, 1930.

sintered by heating for a few minutes to a temperature about 50° C. (90° F.) above the initial deformation temperatures.

Two cones of an arbitrarily chosen standard enamel were placed at diagonally opposite corners of a rectangle, and two of the test enamel at the remaining two corners.

The results obtained were less closely reproducible than those for any of the other tests, and to compensate for this fact a large number of determinations was made and statistical methods were used in analyzing the data. The averages of eight test cones (in no case less than seven) and of an equal number of standard cones were used in determining the cone-deformation temperature for any given batch of enamel. Since all enamels studied were made in triplicate batches, 48 cones were tested to obtain the reported value for any given enamel.

(b) ANALYSIS OF RESULTS

Use was made of the standard cones to reduce all determinations to a common basis in the following way: The deformation temperatures of 242 standard cones were arranged graphically according to their frequency distribution. This arrangement showed a symmetrical distribution in which the arithmetical mean, the median and the mode (the latter being determined graphically) all virtually coincided at 677.5° C. (1,252° F.). Each determination was then corrected by the formula:

$$T_c = T_t - T_s + T_S$$

in which:

T_c = corrected deformation temperature.
T_t = mean deformation temperature of the eight test cones under consideration.
T_s = mean for the eight corresponding standard cones.
T_S = mean deformation temperature of 242 standard cones.

By this method better agreement was obtained between separate determinations on a given enamel composition, and also between separate determinations of the variation in deformation temperature caused by the change from one composition to another.

The results of the cone-deformation test are shown in Table 1 and in Figure 3. The mean rise in cone-deformation temperature due to the A–D, B–E, and C–F changes in composition is 8° C. (14° F.). Since each point given in the figure represents a mean value based upon results obtained with 24 test cones, corrected by 24 standards, the mean temperature rise of 8° C. given above is based upon the results obtained with 288 cones, half of which were test cones and half standards. Each of the other mean values given in the following discussion which applies to Figure 3 is likewise based upon the data obtained with 288 cones. The mean elevation in cone-deformation temperature resulting from the D–G, E–H, and F–I changes in composition was 5° C. (9° F.). Thus the second substitution of 5 per cent silica for 5 per cent feldspar was somewhat less effective than the initial substitution in elevating cone-deformation temperatures, although this was not true in the case of temperatures of maximum heat absorption and initial softening points.

With reference to the substitution of boric oxide for sodium oxide, it is seen that the mean elevation in deformation temperature caused by the A–B, D–E, and G–H changes in composition was 27° C. (49° F.). The mean elevation caused by the B–C, E–F, and H–I

changes was 20° C. (36° F.). Thus while the initial substitution of 3 per cent boric oxide for 3 per cent sodium oxide has a distinctly greater effect upon the cone-deformation temperatures than the second similar substitution, the difference is not so pronounced as in the cases of the two previously described tests.

By interpolation it was estimated that a 1 per cent substitution of boric oxide for sodium oxide, beginning with composition A, D, or G, would have about twice as much effect upon the cone-deformation temperature as a similar 1 per cent substitution ending with composition C, F, or I.

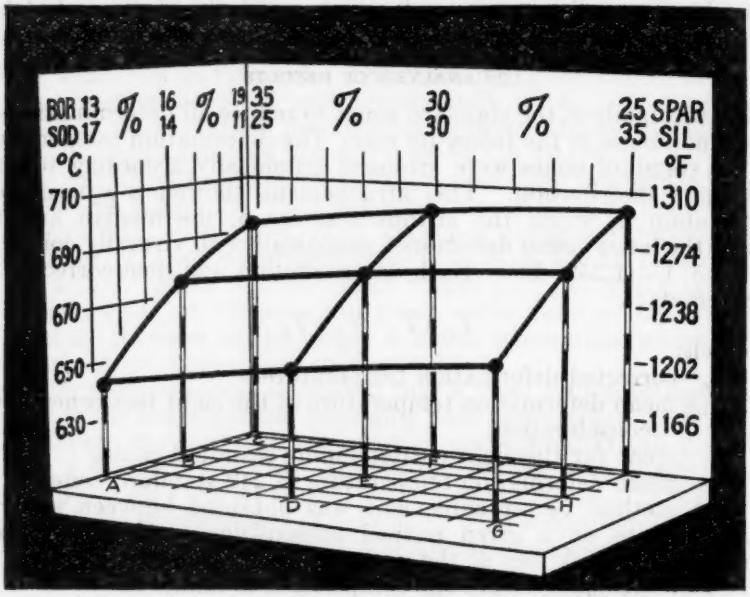


FIGURE 3.—*Variation in cone deformation temperatures with compositions of the enamels*

Key: *SPAR*=Feldspar (considered as a unit).
SIL =Silica added as flint.
BOR =Boric oxide.
SOD =Sodium oxide.

4. BUTTON TESTS

A test of fusion behavior which has had considerable use in determining the fusibility of feldspar, but has had less application in work on enamels, is the "button" test. It consists in heating cylinders of the powdered material and observing the resulting deformation into button-like shapes. For this work, frit, which had been slightly moistened, was formed into cylinders three-fourths inch in diameter and three-fourths inch in length by hand tamping in brass molds.[13] The cylinders were dried before testing. For control purposes cylinders made from the standard enamel were heated simultaneously with each test enamel. The same standard enamel was used as in the

[13] The technique used in this test was based upon that worked out by B. A. Rice while a fellow at the Mellon Institute for the Standard Sanitary Manufacturing Co.

case of the cone-deformation tests. The similarity of procedure was carried further in that four cylinders, two of a test enamel and two of the standard, were placed in the furnace at one time. They were arranged with their centers at the four corners of a 1½-inch square on a piece of one-eighth inch cast iron, coated with TiO_2 powder to prevent sticking.

(a) VARIABLE-END-POINT PRINCIPLE

The manner of using this test, which has been followed heretofore, is to place a plaque bearing cylinders of two or more enamels which it is desired to compare into a furnace at a given temperature and allow it to remain a given time. The resulting "buttons" are then compared visually according to their relative stages of deformation. Hence in comparing different enamels the time-temperature conditions are constant and the end points vary for the different enamels. The underlying principle of this procedure will be referred to here

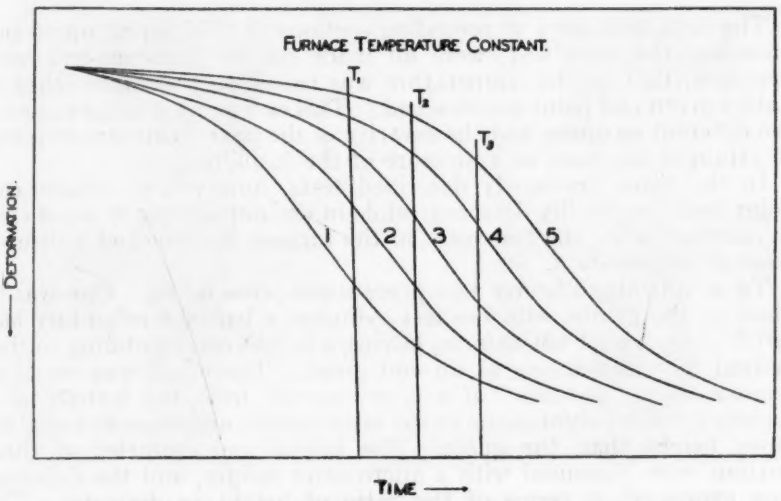


FIGURE 4.—*Illustrative diagram, showing approximately the relative deformation behavior of cylinders of different enamels when treated simultaneously in a furnace at constant temperature*

as the variable-end-point principle. The enamels were first tested according to that procedure, and for purposes of correlation the stage of deformation of each enamel was numerically evaluated by measuring the height and diameter of the buttons of that enamel after the specified heat treatment. When the results were plotted in a solid diagram, as in the case of Figures 2 and 3, the shape of the resulting surface varied, depending upon the time-temperature conditions which happened to be chosen for the comparison. By selection of the test conditions the shape of the figure could be made to vary from wholly convex (with gradual variation in the extent of convexity from one end to the other) through partly convex and partly concave to wholly concave (with gradual variation in the extent of concavity from one end to the other). The reason for these varying relationships may be seen from the diagram shown in Figure 4. The numbered curves in this figure correspond to enamels of different fusibilities .No. 1 being the most fusible. If the extent of deformation

of the respective enamels is compared at the time T_1, the relation between enamels will be different than if compared at T_2 or T_3, and the latter two comparisons will also differ from each other. This effect is produced by the fact that the deformation progresses first slowly, then rapidly, and then slowly again as the buttons flatten, giving a typical **S** curve. Hence one unit of change in shape at a given stage of the deformation is not comparable with one unit at a different stage of the deformation, and it is misleading to make correlations in which these irregularities are ignored.

While tests based on the variable-end-point principle are quickly and easily carried out, and may quite possibly give all the information which is usually desired from a shop test, it was concluded that such tests are unsuitable for the purpose of correlating properties quantitatively with systematic variations in composition.

(b) CONSTANT-END-POINT PRINCIPLE

The tests described in preceding sections of this paper, up to and including the cone test, were all made on the constant-end-point principle; that is, the temperature was raised on a definite schedule until a given end point was reached. This end point was the same for the different enamels, and the severity of the heat treatment required to attain it was used as a measure of the fusibility.[14]

In the three previously described tests, however, a definite end point could be readily detected, while in the button test it is not easy to estimate when the test piece in the furnace has reached a definite stage of deformation.

To avoid this difficulty two precautions were taken. One was to place on the plaque with the test cylinders a bar of a refractory material which would not deform, having a height corresponding to that desired for the buttons as an end point. The effort was made to remove some "buttons" of a given enamel from the furnace at a slightly greater height, some at the same height, and some at a slightly lower height than the guide. The height and diameter of these buttons were measured with a micrometer caliper, and the deformation expressed in terms of the ratio of height to diameter. The selected end point was a ratio of 0.6, and when the several ratios for the respective buttons of a given test enamel were plotted against the corresponding temperatures of removal from the furnace, it was possible to determine by interpolation the temperature required to attain the exact end point selected.

The buttons of the standard enamel were used to reduce all the tests to a common basis in the following ways: Since the test buttons were all brought to approximately the same stage of deformation by means of different degrees of heat treatment, the simultaneously tested buttons of the standard enamel reached various stages of deformation. The respective deformation values for all the buttons of the standard enamel were plotted against the corresponding temperatures of removal from the furnace. Then, in making the graphs for interpolation referred to above, instead of using the observed end temperatures, in each case corrected temperature values

[14] The question logically arises as to what the effect may be of choosing different end points (for example, different degrees of deformation) upon which to base comparisons, any given comparison, however, being based on the constant-end-point principle. The effect of such a procedure is brought out in the discussion accompanying Figure. 7.

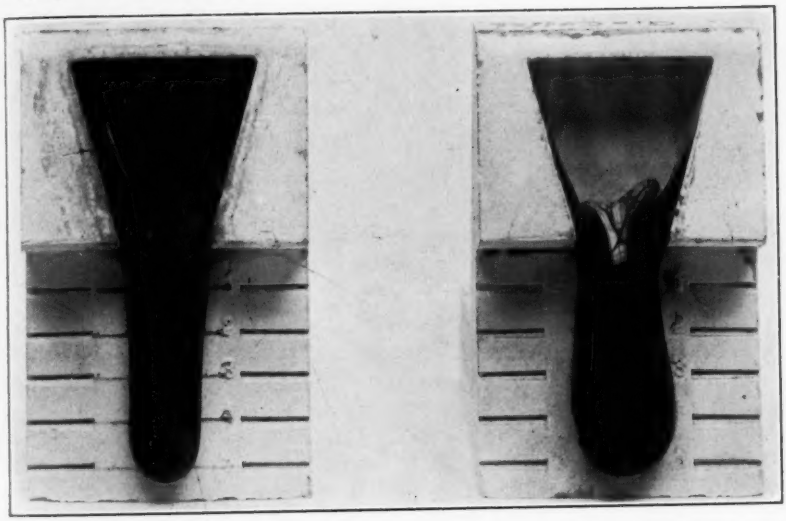


FIGURE 5.—*Two specimens tested by the fusion block method*

The one at the right (dry packed) reached the stage shown at approximately 15°C. (27°F.) lower than the specimen at the left (wet packed), although the enamel was the same in both cases. Note that in the case of the dry-packed block the enamel stream is wider and the receptacle has been left clean.

UNIV. OF MICH.

obtained from the standard enamel curve were used. To obtain these corrected values for the buttons of a given test enamel, the degree of deformation of the simultaneously tested buttons of standard enamel was measured, and the corresponding temperatures were read from the standard enamel curve. The corrected values sometimes differed slightly from the observed temperatures, and gave a more symmetrical relation with the enamel compositions.

The temperatures given in Table 1, when arranged in a space diagram gave a figure similar in appearance to Figure 3, falling approximately 50° C. (90° F.) higher on the temperature scale, and differing somewhat as to the detail of dimensions. The mean rise in end temperature due to the A–D, B–E, and C–F changes in composition was 8° C. (14° F.), and that due to the D–G, E–H, and F–I changes was 7° C. (13° F.). The mean effect of the A–B, D–E, and G–H changes in composition was to raise the determined temperature 29° C. (52° F.), and that of the B–C, E–F, and H–I changes was a further increase of 24° C. (43° F.). Each of these mean values is based upon tests of 36 buttons of the test enamel corrected by 36 of the standard. Here again, the substitution of silica for feldspar causes a moderate and approximately uniform increase in deformation temperature, while the substitution of boric oxide for sodium oxide causes a more rapid change, which diminishes somewhat for each percentage of substitution as the substitution progresses.

5. FUSION BLOCK TESTS

Another test designed initially for use on feldspars, but which has been applied also to the study of the fusion characteristics of enamels, involves the use of "fusion blocks" (see fig. 5), which are made of porcelain and are available commercially.

As in the case of the button tests, the usual practice has been to compare enamels on the variable-end-point principle, by placing two fusion blocks packed with the respective enamels together in a furnace at constant temperature and removing them for comparison when the more fusible one has flowed to the lowest graduation mark. Here again this practice was rejected in favor of the constant-end-point principle, in accordance with which the temperature was increased on a definite time schedule, and the end point taken as the temperature at which the test enamel flowed past a given graduation mark. Both the temperature at which the uppermost graduation mark was passed (the "start" temperature) and that at which the lowest graduation mark was passed (the "finish" temperature) were recorded in this case.

In analyzing the original set of data some discrepancies were observed which resulted in studying the manner of packing the enamel into the receptacles. It was observed that the greatest difference in results existed between specimens which had been moistened and packed very tightly and those which were dry packed. Before testing the dry-packed specimens, the loaded fusion block was placed horizontally in a furnace and the enamel sintered just sufficiently to hold it in place. When the enamel powder was moistened before packing it remained in place, even after drying, without the sintering treatment. When tested, the dry-packed specimens flowed at a lower temperature and in a broader stream than the wet-packed ones, leaving the receptacles free from enamel, as shown in Figure 5.

Thus to secure results which could be compared one with another it was necessary to pack the different specimens uniformly. It is thought that uniformity can be secured more easily by dry packing, but it was not considered necessary to repeat the tests on that basis. The more serious of the original discrepancies were avoided by eliminating a few specimens which by the peculiar character of the enamel streams indicated that the packing had not been consistent with that of the majority of the specimens. Such vacancies in the data were filled by the testing of additional specimens.

The results are shown in Table 1 and Figure 6. Each of the mean temperatures shown in Table 1 is based upon six individual deter-

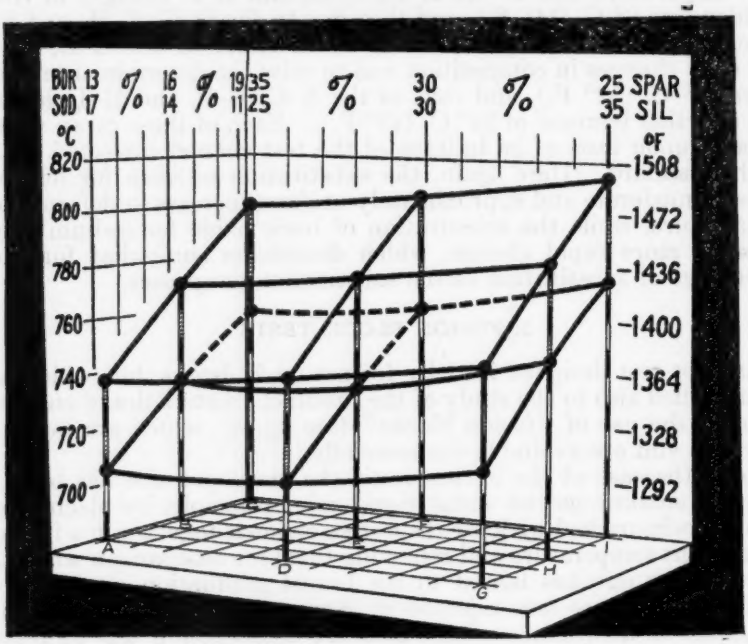


FIGURE 6.—*Variation in "start" and "finish" temperatures of fusion block determinations with the compositions of the enamels*

The lower surface represents "start" and the upper surface "finish" temperatures. The lengths of the intervening pillars indicate the difference between these two temperatures for the respective enamels.

Key: *SPAR* = Feldspar (considered as a unit).
SIL = Silica added as flint.
BOR = Boric oxide.
SOD = Sodium oxide.

minations, two on each of the enamels made in triplicate. The individual determinations varied from the means by an average of 4° C. (7° F.), and a maximum of 11° C. (20° F.).

Figure 6 shows the relation between composition and (1) "start" temperature, (2) "finish" temperature, and (3) spread between "start" and "finish" temperatures. For the A, D, and G compositions the mean spread is 34.3° C.; for B, E, and H, 37.7° C.; and for C, F, and I, 41.0° C. Thus the mean increase in spread from enamels A, D, and G to B, E, and H is 3.4° C., and the mean further

increase to C, F, and I is 3.3° C. These latter two mean values are each based upon the results of 72 temperature determinations.

Since the temperature was increased in these tests according to a definite schedule, an increased temperature interval indicates also an increased time interval. Thus it is apparent that as boric oxide was substituted for sodium oxide, not only did the flow begin at a higher temperature, but once begun it proceeded at a slower rate in spite of the increased temperature. Hence the viscosity at corresponding stages of flow must have been greater. Also, since there is experimental evidence from other sources that the substitution of boric oxide for sodium oxide increases the firing range,[15] it is not unreasonable to assume that the spread between "start" and "finish" temperatures in this test may be an indication of the firing ranges of the enamels under study.

The "finish" temperatures were in better agreement than the "start" temperatures. Considering the effect upon "finish" temperatures of substituting silica for feldspar, it is seen that the A–D, B–E, and C–F changes in composition caused a mean rise in "finish" temperatures of 5.7° C. (10° F.), while the D–G, E–H, and F–I changes caused a mean rise of 9.3° C. (17° F.).

The substitution of boric oxide for sodium oxide was, as in previously described tests, more effective than the feldspar-silica substitution in changing the property under study. The A–B, D–E, and G–H changes caused a mean elevation in "finish" temperature of 33.3° C. (60° F.), while the B–C, E–F, and H–I changes caused a mean elevation of 29.0° C. (52° F.). As may be seen in Figure 6, the "finish" temperatures have almost straight line relations with the enamel compositions. The data indicate, however, that the lines do actually deviate from straightness in approximately the same manner as, but to a lesser degree than, in the previously discussed cases. By interpolation it was estimated that an increase in boric oxide from 13 to 14 per cent, at the expense of sodium oxide decreasing from 17 to 16 per cent would cause an increase in the determined temperature of about 12° C. (22° F.) while a similar increase from 18 to 19 per cent at the expense of sodium oxide decreasing from 12 to 11 per cent would cause an elevation of 9° C. (16° F.).

V. CORRELATION OF FUSION TESTS WITH EACH OTHER AND WITH FIRING BEHAVIOR OF THE ENAMELS

There is a systematic relation between the results of the five tests which have been described. The increase of silica, at the expense of feldspar caused, according to all of these tests, a moderate increase in refractoriness, averaging around 1° to 1.5° C. (1.8° to 2.7° F.) for each 1 per cent substitution. The curves representing this relation deviate slightly from a straight line, but hardly enough to invalidate the preceding generalization.

The substitution of boric oxide for sodium oxide falls in a different category. The first substitution, embracing the A–B, D–E, and G–H changes in composition, caused in all tests a decided increase in the determined temperatures, approximating 30° C. (54° F.) for a 3 per cent substitution. The second substitution, embracing the

[15] Danielson, R. R., and Sweely, B. T., Relation Between Composition and Properties of Enamels for Sheet Steel, J. Am. Cer. Soc., vol. 6, No. 10, p. 1011, 1923.

B–C, E–F, and H–I changes caused a further increase which varied in magnitude with the temperatures involved. In general, for the tests having lower end temperatures, the rise caused by this second composition change was only about one-third that caused by the first, but this ratio increased with the end temperatures of the tests until, at the fusion block finish temperatures, the rise was about seven-

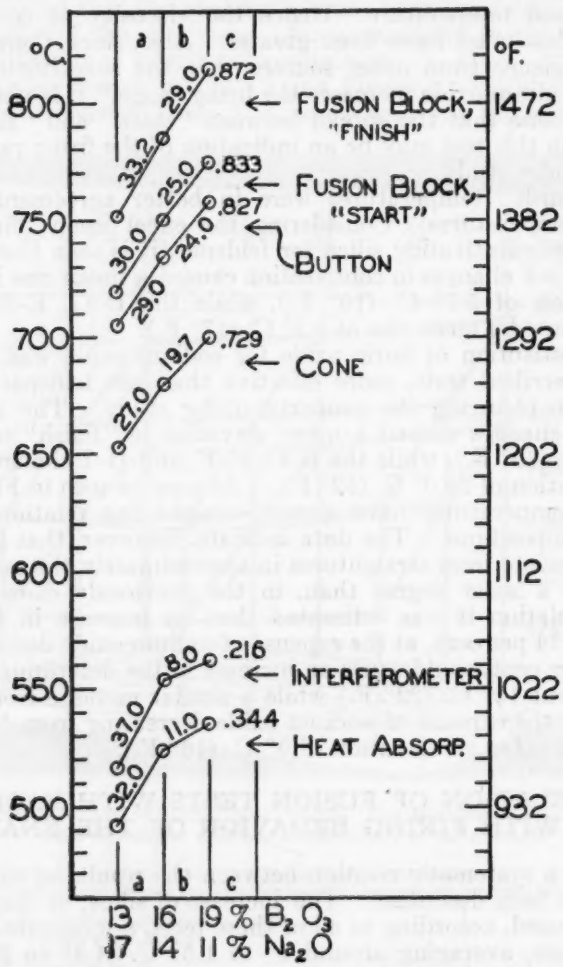


FIGURE 7.—*Effect of temperature at which end point occurs upon change of end point with enamel composition*

The "labels" of the curves indicate the respective types of test involved. Note that the curves become straighter with increasing temperature.

eighths of that caused by the first substitution. This relation is shown in Figure 7, in which there are six groups of three connected points. The three points in each case correspond to three different percentages of boric and sodium oxides, as shown on the abscissa. The ordinate shows for the respective tests the mean of the determined temperatures for all enamels having the indicated percentages of boric

and sodium oxide. Thus the points at the left are means for the A, D, and G compositions, those midway for the B, E, and H, and those at the right for the C, F, and I compositions. As indicated in the figure, each set of three points pertains to a different kind of test. The numbers in columns *a* and *b* indicate in °C. the temperature increases corresponding to the changes in composition shown on the abscissa. In column *c* are given the ratios of the *a* to the *b* increases, which will be referred to as the "*c* ratios." It is apparent that, in general, the higher the temperature at which the end point occurs, the higher the *c* ratio.[16]

It is not necessary to search far for a reasonable explanation of why there should be a systematic change in the *c* ratio with temperature. The bottom group of three points in Figure 7, relating to temperatures of maximum rates of heat absorption, represents determinations which involve no flow of the enamel whatever. The next higher group, relating to initial deformation points as indicated by the interferometer, represents determinations involving only an almost infinitesimal amount of flow, which may be disregarded. These two types of determinations, therefore, may be considered as involving fusibility, uninfluenced by viscosity. The remaining types of determinations involve not only fusibility, but also viscosity, and they are therefore influenced by the time required for the enamels to flow from one position to another.

If the rate of flow from the beginning of flow to the end point were uniform in any particular test for all the enamels studied, obviously whatever end points were chosen would bear the same relation to one another as the temperatures at which flow started, which are indicated by the interferometer test. But since the flow is slower for the compositions having higher ratios of boric oxide to sodium oxide, the end temperatures for those compositions are displaced upward on the temperature scale relative to the more rapidly flowing compositions. The greater the amount of flow involved the greater the displacement. This condition operates progressively to straighten the lines connecting the various groups of points as the amount of flow involved increases from virtually none at the initial deformation temperatures to a very considerable amount at the fusion block finish temperatures.[17]

The question naturally arises as to whether any or all of the tests which have been described indicate the relative behavior of the enamels when actually fused as coatings on sheet iron. It has been reported that in some instances enamels which appear in a certain order of "flowability" when tested at lower temperatures will reverse this order when tested at considerably higher temperatures.[18] This observation is in harmony with the fact that the viscosities of different

[16] Although the lines connecting the points in Figure 7 are drawn straight, there is no reason to assume that a sharp break in properties actually occurs. The true relation is thought to be better depicted in Figures 2, 3, and 6. The ratios obtained by interpolation from such figures (given earlier in the text) are in even greater contrast than those cited above, which are based upon the uninterpolated data.

[17] The above explanation answers the question raised in footnote 14 as to the influence of the choice of end point upon the results obtained when using the constant-end-point principle. Each of the five tests was carried out on this principle, and each has a different end point. The results of any one test give a cross section showing the relation between enamels of the respective compositions at a given stage of the process of "fusion." A number of such cross sections are required, as in Figure 7, to complete the picture. These several cross sections constitute a framework upon which a three dimensional figure could be readily constructed, if desired, bringing the whole set of relations into representation by a single continuous surface, which could be used for interpolation between the established points.

[18] C. J. Kinzie, J. Am. Cer. Soc., vol. 15, No. 6, p. 357, 1932.

glasses do not always remain in the same relative order at different temperatures.[19]

Each of the enamels used in this study was fired on test pieces in the laboratory under a variety of conditions of temperature and time. Due to the fact that a workable enamel may be fired satisfactorily within a comparatively wide range of conditions, it was impracticable to establish optimum firing temperatures closely enough to determine whether the tests giving a lower "*c* ratio" or those giving a higher "*c* ratio" were more indicative of the firing behavior of the enamels. The establishment of such ratios requires the accurate location of the several temperatures involved, and it is probable that only an accumulation of observations under various plant conditions will determine which of these tests best gives the information desired in any particular case. The firing ranges of the respective enamels did, however, accord with the general pattern followed by all of these tests in which the substitution of feldspar for silica caused a moderate increase in fusibility, and the substitution of sodium oxide for boric oxide caused a considerably more marked increase in fusibility. It appears, therefore, that at least in so far as these particular enamels are concerned, the indications of the described tests are not subject to any general reversals when applied to actual working conditions.

VI. SUMMARY AND CONCLUSIONS

The compositions of nine ground coat enamels for sheet iron were varied within a region approximating commercial practice by substituting silica (added as flint) and feldspar one for another while the percentages of other ingredients remained constant, and by substituting boric oxide and sodium oxide one for another, while the percentages of other constituents remained constant. In two other enamels the above-named fluxes were varied as a unit against the two refractories as a unit. The fusion properties of the enamels were studied through five different tests, namely, (1) temperature of maximum heat absorption, (2) softening temperature as observed with the interferometer, (3) cone deformation temperature, (4) button deformation temperature, and (5) fusion block deformation behavior.

The following conclusions, applicable within the limits of composition studied, were drawn:

1. The increase of silica from 25 to 35 per cent with simultaneous reduction of feldspar from 35 to 25 per cent, caused a moderate increase in refractoriness. The full 10 per cent substitution raised the end temperatures of the different tests by 10° to 15° C. (18° to 27° F.), or an average of 1° to 1.5° C. (1.8° to 2.7° F.) for each percentage of change in composition.

2. The increase of boric oxide from 13 to 19 per cent with simultaneous reduction of sodium oxide from 17 to 11 per cent caused an increase in end temperatures of the various tests which was quite marked in the region near 13 per cent boric oxide, and which became less perceptible as the boric oxide content approached 19 per cent. This diminution in effectiveness was most conspicuous in the tests involving no flow of the specimens, and became less prominent as

[19] G. S. Fulcher, J. Am. Cer. Soc., vol. 8, No. 6, p. 339, 1925. E. W. Washburn, G. R. Shelton, and E. E. Libman, U. of Ill. Bull., vol. 21, No. 33, 1924.

the amount of flow involved in the respective determinations increased. The maximum diminution of effect with successive substitutions occurred in the case of the initial deformation temperature determinations by the interferometer method, in which a 1 per cent increase in boric oxide from 13 to 14 per cent (with corresponding decrease in sodium oxide) caused an elevation in the end temperature estimated by interpolation to be approximately 15° C. (27° F.), while a similar increase from 18 to 19 per cent caused an elevation estimated to be about 1.5° to 2° C. (2.7° to 3.6° F.). The minimum diminution occurred in the case of the fusion block finish temperatures, in which these same two changes in composition caused elevations in the determined temperatures of 12° C. (22° F.) and 9° C. (16° F.), respectively.

3. The reason that the diminution in the effectiveness of successive substitutions of boric oxide for sodium oxide became less noticeable as the amount of flow involved in the respective determinations increased might be traced to the fact that variations in viscosity of the enamels had more opportunity to influence the results of those tests which involved a greater flow of the specimens.

4. Since the tests were conducted on definite time-temperature schedules, the end temperatures of the respective determinations increased with the amount of flow involved. This effect placed the determinations in the following order of increasing temperature: Maximum heat absorption temperature, initial deformation temperature as observed in the interferometer, cone deformation temperature, button deformation temperature, fusion block start temperature, and fusion block finish temperature. These determinations were spread over a range of approximately 300° C. (540° F.) from about 500° C. (900° F.) to about 800° C. (1,470° F.).

5. In conducting tests for the purpose of correlating properties quantitatively with systematic variations in composition, it is desirable to avoid the "variable-end-point" principle, according to which all specimens are treated alike and the various degrees of effectiveness of the treatment in the respective cases noted. The use of this principle makes the apparent relationships irregular, variable, and dependent upon chance to a much greater extent than is the case when using the "constant-end-point" principle, according to which the extent or intensity of treatment required to produce a given effect is the basis of comparison.

6. While the results of this study do not warrant the statement that any one of the described tests gives a truer picture of the behavior of the enamels in practice than another, they do indicate that the general pattern covering the results of all the tests, as outlined in conclusions 1 and 2, is indicative of the relative behavior of the enamels in process of fusion on metal.

WASHINGTON, April 16, 1932.

R P 525

THE PHOTOGRAPHIC EMULSION: THE MECHANISM OF HYPERSENSITIZATION

By Burt H. Carroll and Donald Hubbard

ABSTRACT

Confirming earlier work at the Bureau of Standards, hypersensitization by bathing with ammonia is shown to consist of a selective increase in sensitivity for the spectral region of sensitization by the dye. Hypersensitization by a given solution is highly dependent on the dye and to a less extent on the emulsion; for many commercial panchromatic emulsions, water is preferable to ammonia solutions for practical use. On bathing a photographic emulsion in a solution there is set up a membrane equilibrium which is shown by electrode measurements to obey the Donnan equation. As a result of an almost unique combination of properties, bathing with ammonia and drying leaves an emulsion with an excess of silver over halogen; this is confirmed by chemical analysis of plates and baths used for hypersensitization. Comparison of data on the effect of ammonia on sensitization by known dyes with those of Research Paper 488 on the effect of silver ion concentration in the emulsion on the same dyes shows very close correspondence. There is satisfactory correlation between the photographic effects of ammonia treatment and those of excess silver in the emulsion; other theories of hypersensitization, which are discussed briefly are shown to be inadequate. Reports of hypersensitization by hydrogen peroxide are shown to be the result of inadequate control experiments, but appreciable hypersensitization by reducing agents was confirmed.

CONTENTS

	Page
I. The phenomena of hypersensitization	211
II. The equilibrium between photographic emulsions and ammonia solutions	216
III. Correlation of the chemical and sensitometric data on hypersensitization	221
IV. Acknowledgment	227
V. List of references	227

I. THE PHENOMENA OF HYPERSENSITIZATION

Silver halides emulsified in gelatin selectively absorb radiation of the shorter wave lengths; for bromiodide, the absorption is very small for wave lengths greater than 500 mμ, and for other halides the limit is shorter. Photographic sensitivity necessarily corresponds to the absorption. As discovered by Vogel in 1876, certain dyes which absorb the longer wave lengths may sensitize silver halide emulsions for these regions. This increase in sensitivity for the region absorbed by the dye is, however, almost invariably accompanied by a decrease in the short wave length sensitivity of the emulsion. The magnitudes of both these changes are involved in a determination of the effectiveness of sensitization in a given case. In the comparison of the sensitization of a given emulsion by a given dye under varying conditions, which was the principal determination

made in the experiments described in this paper and in our preceding communication (Research Paper No. 488) we found two of the three possible general types of change. Long and short wave length sensitivity may increse or decrease together, the change in the ratio of sensitivity to the two regions being less than the changes in absolute values. The long wave length sensitivity may increase or decrease with relatively constant short wave length sensitivity, and correspondingly large changes in relative spectral sensitivity. The third case of constant long wave length sensitivity and varying short wave length sensitivity has not been encountered. Change in the absolute values of sensitivity for both long and short wave lengths with constant relative spectral sensitivity was first reported by Sheppard (1)[1] as a result of sensitization by allyl thiocarbamide, or desensitization by chromic acid, these procedures involving, respectively, the formation and destruction of sensitivity nuclei. The writers have found similar effects (2), although the fractional change in long wave length sensitivity was generally the smaller. Changes in hydrogen ion, or even more in silver ion concentration in the emulsion (2) tend to increase the long wave length sensitivity with little change in the short wave length sensitivity. In contrast to the first case, the relative spectral sensitivity is greatly changed.

The discovery that sensitization by a dye could be improved by changing conditions in the emulsion was first made by Schumann (3), who found that a preliminary bath of ammonia improved sensitization by cyanine; in spite of numerous other suggestions, ammonia is still the most important hypersensitizing agent. We shall use the term "hypersensitization" to cover any case in which increase in sensitization by a dye is produced by treatment with a material itself colorless or absorbing a spectral region different from that of the dye. The term has been most commonly applied to after treatment of plates or films sensitized in the emulsion, but the mechanism appears to be the same whether the hypersensitizing agent is applied before, with or after the dye, and there is generally little difference in the magnitude of the effect.

Hypersensitization of course implies an increase in sensitivity to the longer wave lengths. In spite of the numerous investigations of the subject, there is still some dispute as to whether the sensitivity for the shorter wave lengths is normally increased. In the latest edition of Eder's Ausführliches Handbuch der Photographie, Dieterle (4) states that the change in this region is relatively small. Experiments at this bureau (5) (6) have been in entire agreement that hypersensitization normally involves a great increase in relative sensitivity to the longer wave-lengths; the data of Walters and Davis (6) are particularly clear on this point. However, Wall (7) reported that in a "long series of experiments where there was so-called increased color sensitiveness, there was also increased general sensitivity, and if the ratio of the blue to the color sensitiveness was taken into account, there was practically no increase in the same." We are, therefore, including in this paper data which demonstrate that in our experiments hypersensitization always involved an increase in relative sensitivity to the longer wave lengths.

[1] Numbers in parentheses here and throughout the text refer to the list of references at the end of the article.

These data also show a fact which has been imperfectly understood: That a given treatment may produce marked hypersensitization in one plate or film, and none in another. These differences are to be attributed primarily to the dye and secondarily to the emulsion. The data of Walters and Davis (6) for example, show clearly that the isocyanine dyes, pinaverdol, and orthochrome *T*, were hypersensitized very little by ammonia, while it produced a large effect on sensitization by pinacyanol, and a still larger one on sensitization by dicyanine. Jacobsohn (8) has reported that a neutral emulsion could be readily hypersensitized by ammonia, while a comparable emulsion made by the ammonia process could not. Other illustrations could be given, but these will serve to make the point that it is impossible to say that a given bath will or will not cause hypersensitization without specifying the dye and emulsion. Some of the confusion on this point has probably risen from the varying requirements of users; in certain types of spectrography, for example, all other properties may be sacrificed to sensitivity, and it is possible to work with plates having fog which would be intolerable for pictorial use. The use of various methods of testing, some of them quite imperfect, have added to the misunderstandings.

The most serious error in some studies of hypersensitization has been the lack of adequate controls. The great majority of panchromatic emulsions are considerably improved in sensitivity to the longer wave lengths simply by washing with water ((6) and Table 1). It is therefore essential that the hypersensitizing action of any solution should be compared with that of water, under the same conditions of bathing and drying. If the emulsion is compared only without treatment, and after treatment with a given solution, effects which are actually caused only by the water of the solution may be ascribed to the dissolved substance.

In these experiments, sensitivity was determined by nonintermittent exposure in the sector-wheel sensitometer through appropriate filters to isolate spectral regions absorbed by the dye and by the silver halide. In a few cases, the sensitivity conferred by the dye was such a small fraction of the total that exposure to white light could be substituted for exposure to blue light without serious error. Sensitivity has been reported in terms of speed numbers $(10/i)^2$ corresponding to development to a constant γ. This was 1.0, unless the emulsion was of high contrast, when a value in the working range was chosen.

The plates or films were bathed for about three minutes at a temperature of 10° to 15° C. with constant rocking, and dried in a rapid current of air. The drying should be rapid. Unless the air temperature is less than 25° C. and the humidity at a low relative value—such as exists in heated rooms in cold weather, it is desirable to accelerate the drying by soaking the plate in alcohol for a few minutes after bathing. This treatment unfortunately can not be applied to most films. The entire emulsion surface was exposed to the air current in our drying apparatus; it is important that no part of it

[1] In the values of inertia (i) no correction was made for the absorption by the filter, so that the speed numbers are comparative only. This results, for example, in low values of speed numbers for blue light, since the transmission of the "C" filter is not over 27 per cent for any wave length.

should be shielded by the plate rack or other obstruction if the dried plate is to be uniform in sensitivity.

Table 1 gives data on the hypersensitization of six fast commercial panchromatic emulsions. Similar data for another emulsion may be found in the control experiments recorded in the first three lines of Table 7. Exposures to "blue" light were made through the Wratten C filter, those to "red" light through the Wratten A, in both cases in addition to the Davis-Gibson correction filter. In three cases, plate B and films B and C, two emulsion numbers are represented in the comparisons of the washed emulsion with the untreated and ammonia-treated emulsion, respectively.

TABLE 1.—*Hypersensitization of commercial panchromatic plates and films*

Emulsion	Bath	Halide extracted by bath, molar ratio to AgBr × 1,000		Speed at γ=1.0		Fog for 6-minute development
		Br−	Cl−	Red light	Blue light	
Plate A	None			82	74	0.39
	Water	5.2	10.5	173	57	.41
	0.05 *N* NH_3	7.5	11.6	195	58	.44
Plate B:						
Emulsion 2	None			43	35	.28
	Water			85	31	.33
Emulsion 1	...do	1.6	64	42	13	.27
	0.25 *N* NH_3	8.4	63	59	19	.42
Plate C	None			15.5	20.5	.21
	Water	.7	0	17	22	.23
	0.5 *N* NH_3	5.2	0	51.5	39	.42
Film A	None			17	34	.23
	Water	5.8	38	51		.23
	0.25 *N* NH_3	15.4	38	50	50	.29
Film B:						
Emulsion 1	None			23	37	.23
	Water	9.9	35	102	69	.24
Emulsion 2	...do	8.8	38	60	43	.21
	0.25 *N* NH_3	17.6	35	100	60	.21
Film C:						
Emulsion 2	None			40	38	.19
	Water	4.5	13	70	56	.20
Emulsion 1	...do	3.7	0	57	40	.21
	0.25 *N* NH_3	17.3	0	100	30	.72

Several observations may be made on these data. In the first place, the increase in red-light speed was invariably greater than the increase in blue-light speed, so that the relative sensitivity to the longer wave lengths increased. This is in agreement with previous experiments at this bureau, and in contradiction to Wall's statement. The sensitivity to blue light normally was increased,[3] but the increase was comparable with that in red-light speed in only two cases (ammonia treatment of pl. B and film B).

The second point of interest is that treatment with water alone was almost as effective as the use of ammonia solutions, with the one ex-

[3] Pl. A shows the unusual and unexplained effect of a decrease in sensitivity to blue light on washing; the change is small, but apparently real. The decrease in film C on ammonia treatment is obviously the result of the heavy fog which was produced.

ception of plate C.[4] The difference between water and ammonia was much more marked for the panchromatic emulsions tested by Walters and Davis (6) and for some of our experimental emulsions sensitized with known dyes, recorded in Tables 2, 3, and 5. Spectrograms indicate that the dyes now used for sensitization are different from those in use only a few years ago. As the use of water involves less risk of causing fog than the use of ammonia, especially if the plates are to be kept any time after bathing, it is preferable for most cases. The increase in speed which is obtainable even from the fastest panchromatic emulsions by simple bathing with cold water is evident from the data.

TABLE 2.—*Hypersensitization of experimental emulsion 4–143*

[Speed numbers are relative only, the correction filter having been omitted in these tests; all values are for development to $\gamma=1.0$]

Bath	Speed numbers		
	Unsensitized emulsion	Pinacyanol-sensitized emulsion	
	Blue-light exposure	Blue-light exposure	Red-light exposure
None	18.5	12.5	70
Water	22	17	165
0.001 *M* N_2H_4	27	17.5	250
0.25 *M* NH_3	53	39	800

TABLE 3.—*Hypersensitization of experimental emulsion 4–145*

[Speed numbers are relative only, the correction filter having been omitted in these tests; all values are for development to $\gamma=1.0$]

Bath	Speed numbers		
	Unsensitized emulsion	Pinacyanol-sensitized emulsion	
	Blue-light exposure	Blue-light exposure	Red-light exposure
None	45	23.5	55
0.001 *M* N_2H_4	47	45	365
0.25 *M* NH_3	89	110	635

The magnitude of the change in sensitivity to blue light is of considerable importance in deciding on the mechanism of hypersensitization. In panchromatic emulsions, it is generally larger than would be expected from the fact that many unsensitized emulsions are practically unaffected by washing or ammonia treatment. Moderate speed commercial emulsions (Seeds 23, Eastman 33 and 36), and comparable experimental emulsions showed no increase in speed on bathing in ammonia, although other unsensitized experimental emul-

[4] Reference to column 3 shows that pl. C contained an unusually small amount of soluble bromide. This accounts for the constant sensitivity on washing. The data on bromide extracted by the ammonia solutions will be discussed later in the paper. The increase in red-light speed of film C on ammonia treatment was accompanied by an increase in fog which made the film practically useless.

sions have given positive results. The experiments recorded in Table 2 and 3 demonstrate that the sensitizing dye changes sensitivity to blue light, although it does not sensitize for this region. The emulsions used for these experiments were made by the neutral process differing only in that the silver iodide was 1 per cent of the total silver in 4–143 and 4 per cent in 4–145. After washing, potassium bromide in the molecular ratio of 5 KBr per 1,000 AgBr was added to each emulsion, and they were digested to rather less than maximum sensitivity. Each emulsion was coated in two portions, one unsensitized and the other with the addition of pinacyanol. After drying, plates were treated as indicated in the tables and tested. The tables show that the pinacyanol, plus the soluble bromide, reduced the sensitivity of the emulsions to blue light. On washing with water which removed the soluble bromide, the blue-light sensitivity of the pinacyanol-sensitized portions was restored to the original value; that of the unsensitized portion was only slightly increased, as would be anticipated from the relatively small effect of silver ion concentration on sensitivity in the absence of dyes (9). The increase in blue-light sensitivity on washing the commercial emulsions recorded in Table 1 may therefore be interpreted as the removal of a desensitizing effect, since all dyes in the presence of bromide cause some desensitization to the blue. Emulsions 4–143 and 4–145 (Tables 2 and 3), probably because of incomplete digestion, increased in speed on ammonia treatment of the unsensitized portions; the blue-light speed of the sensitized portions increased in about the same ratio. In all cases, the increase in red-light speed was much greater than the increase in blue-light speed.

In order to understand the photographic effects produced by bathing with ammonia, it will be necessary first to consider the chemical equilibrium set up by this process.

II. THE EQUILIBRIUM BETWEEN PHOTOGRAPHIC EMULSIONS AND AMMONIA SOLUTIONS

If two solutions are separated by a membrane which is permeable to the solutes, diffusion through the membrane will ultimately bring the concentrations on both sides to the same values. If, however, there is present in one of the solutions an ion which can not diffuse through the membrane, this will result in an uneven distribution of all the ions between the two sides of the membrane when the system has reached equilibrium. Donnan (10) has demonstrated that the equilibrium is governed by the relation that the ratios of concentrations of all diffusible univalent ions of the same sign, on the two sides of the membrane shall be the same, and that the product of the concentrations of any pair of (univalent) positive and negative ions on one side of the membrane shall be the same as the product of the concentrations on the other side.

When a jelly, such as a photographic emulsion, is immersed in a solution, the Donnan equation may be applied to the concentrations of the solution inside and outside the jelly. Let us consider first the case of an emulsion of pure *AgBr* in gelatin bathed in a solution of an alkali, such as *NaOH*. The gelatin is permeable to all the ions of *NaOH* and *AgBr*, so that all four of these will be found both inside and outside the emulsion at equilibrium. However, the gelatin

combines with OH^- to form a negatively charged complex which acts as a nondiffusible ion present only inside the gelatin and thus causes an uneven distribution.

According to Donnan's equation

$$\frac{[OH^-]_o}{[OH^-]_i}=\frac{[Br^-]_o}{[Br^-]_i}=\frac{[Na^+]_i}{[Na^+]_o}=\frac{[Ag^+]_i}{[Ag^+]_o}$$ (where the subscripts i and o indicate the inside and outside solutions, respectively)

$[OH^-]_o > [OH^-]_i$ because of the combination of OH^- and gelatin, so that

$$[Ag^+]_i > [Ag^+]_o \text{ and } [Br^-]_i < [Br^-]_o$$

The excess of positively charged diffusible ions in the gelatin is electrically balanced by tbe negative (gelatin $OH)^-$ complex, and $[Ag^+]_i > [Br^-]_i$. If the emulsion is removed from the solution and dried, it will be left with an excess of Ag^+ over Br^-, the excess Ag^+ being in combination with the gelatin (11); the solution will contain an excess of bromine over silver, since these were originally in equivalence in the emulsion.

Silver bromide being very difficultly soluble, the quantities involved are very small, and it is only by repeated extraction that any considerable excess of silver can be left in the emulsion. If, however, ammonia is substituted for the simple alkali, the solubility of silver bromide is so increased that much larger effects may be produced. The equilibrium is essentially the same although complicated by the second equilibrium

$$\frac{[Ag^+]\times[NH_3]^2}{[Ag(NH_3)_2^+]}=K$$

which results in a decrease in $[Ag^+]$ to a very small value, with corresponding increase in $[Br^-]$ to maintain the condition that $[Ag^+]\times[Br^-]=S$ (solubility product of AgBr). The principal ions in the outside solution are therefore $Ag(NH_3)_2^+$, NH_4^+, Br^-, and OH^-. The same ions, plus the nondiffusible (gelatin-OH)$^-$, are present inside.

$$\frac{[Ag(NH_3)_2^+]_i}{[Ag(NH_3)_2^+]_o}=\frac{[NH_4^+]_i}{[NH_4^+]_o}=\frac{[Br^-]_o}{[Br^-]_i}=\frac{[OH^-]_o}{[OH^-]_i}$$

Ammonia being alkaline, we have, as before, that $[OH^-]_o > [OH^-]_i$ and consequently that $[Ag(NH_3)_2^+]_i > [Ag(NH_3)_2^+]_o$ and $[Ag(NH_3)_2^+]_i > [Br^-]_i$. The concentrations of $Ag(NH_3)_2^+$ and Br^- being much greater than those of Ag^+ and Br^- in simple alkali solutions, an emulsion bathed in an ammonia solution is left with an appreciable excess of $Ag(NH_3)_2^+$ over Br^-. On drying the film the complex ion must decompose, since all known compounds of silver salts and ammonia are in equilibrium at room temperature only with ammonia pressures of the order of 100 mm of mercury. Before drying, the $Ag(NH_3)_2^+$ ions had been electrically balanced by the negative gelatin ion, formed by combination of the gelatin and OH^- ions. As the ammonia is removed, the remaining Ag^+ ions tend to combine with the gelatin ion. In the quantities formed by hypersensitization, the silver gelatin complex is in equilibrium (11) with a silver ion concentration enormously greater than that of the emulsion before treatment. A

normal emulsion contains about 3×10^{-3} g equivalent of AgBr per gram of gelatin; if 1 per cent of this is decomposed by the ammonia treatment, 3×10^{-5} g equivalent of Ag^+ will be combined with 1 g of gelatin; this corresponds at pH 9 with a silver ion concentration of 10^{-6} N as against 10^{-10} N in an average emulsion as coated. In an emulsion bathed with water alone, the final silver ion concentration will probably be less than one-tenth that produced by ammonia.

It will be noted that this final result is dependent on several conditions, which are fulfilled almost uniquely by ammonia and some of the amines. Ammonia gives an alkaline solution which dissolves silver salts by formation of a positively charged complex ion of silver, which breaks down on drying. If the complex ion containing the silver is negatively charged, as in cyanide, thiosulphate, sulphite or thiocyanate solutions, its distribution will follow the same ratio as the bromide ion and there will be no excess of silver left in the emulsion and no hypersensitization.[6] A nonvolatile complex would also prevent the final rise in $[Ag^+]_f$ on drying. The magnitude of the final effect will increase with increasing solubility of silver bromide, and consequently with increasing concentration of ammonia. The presence of soluble bromide reduces the effect of the ammonia, since $[Br^-]_f$ may be greater than $[Ag(NH_3)_2^+]_f$ if there is enough soluble bromide present, even though the ratios of inside and outside concentrations are the same as in the absence of soluble bromide. Conversely, the effect is increased by the addition of silver salts, such as the chloride or oxide, to the ammonia bath. An acid solution dissolving silver salts by formation of a volatile negative complex would produce the same effect as ammonia, but as far as we know, no such solution exists.

The applicability of the Donnan equation to equilibrium between silver bromide-gelatin emulsions and ammonia solutions was demonstrated experimentally. For quantitative results it was necessary to use liquid emulsion, separated from the ammonia solution by a membrane. Ion concentrations can not be measured in the set emulsion on a plate; and because of the volatility of the ammonia and the necessary change in temperature, it was also impracticable to bring the emulsion on a plate to equilibrium, then strip and melt it for measurements. Accordingly, 50 ml samples of emulsions were placed in small sacks of goldbeater's skin or collodion which were surrounded with ammonia solution, the system being maintained at 30.0° C. by an air thermostat. Stoppers into the sack and the outside vessel made it possible to insert into either one a silver-silver bromide electrode and salt bridge to determine the bromide ion concentration, or to remove samples of either solution. The readings taken with the electrode near the membrane were found to be somewhat uncertain, so that the final readings were all taken on samples which had been pipetted into a closed cell. The bromide ion concentration never became entirely constant, even after agitation for 24 hours or more, but the slow drift after this time was apparently caused by hydrolysis of the gelatin in the emulsion by the ammonia, with conse-

[6] One hypothesis as to the mechanism of hypersensitization was that it is caused by intragranular etching of the silver halide grains by the ammonia, with consequent exposure of fresh surface for the dye. Lüppo-Cramer (12) tested this by adding one-half per cent Na_2SO_3 or KSCN to dye baths; we used 0.0034 N KCN, which is equivalent to 0.5 N NH_3, in solvent action for silver bromide. The negative results which were obtained could have been predicted from the failure of these baths to leave the emulsion with excess silver, and the strong adsorption of the anions of these solutions, which would tend to replace the basic dyes.

quent formation of diffusible amino acids whose buffer action in the outside solution reduced the pH difference between the inside and outside; after the first day, the drift in electrode potential became less than 1 mv per day. Readings were then taken on samples from the emulsion and the outside solution both with the silver-silver bromide electrode and the glass electrode (each being compared with a standard calomel electrode). We are indebted to M. R. Thompson, of the chemistry division of this bureau, for making the difficult measurements of hydroxyl ion concentration in these systems with the glass electrode.

If the equilibrium obeys the Donnan equation, then

$$\frac{[Br^-]_o}{[Br^-]_i} = \frac{[OH^-]_o}{[OH^-]_i}$$

Since the potential of either electrode is proportional to the logarithm of the corresponding ion concentration, if these two ratios are equal, the differences in potential of the two electrodes in the emulsion and the outside solution will be the same. The data in Table 4 show that this condition was fulfilled for both membrane materials and over a moderate range of conditions. The variations in the absolute values were caused by the concentration and volume of the emulsion samples and possibly by greater permeability of the collodion. Ammonia concentration was limited to about 0.05 *N* by the decreasing accuracy of the glass electrode at higher alkalinities.

TABLE 4.—*Equilibrium between AgBr-gelatin emulsions and ammonia solutions (originally 0.050 N) at 30.0° C.*

[Emulsions inside membrane, ammonia solution outside]

Membrane	[OH⁻]		[Br⁻]		Potential difference of electrodes outside and inside (in millivolts)	
	Outside	Inside	Outside	Inside	Glass electrode	Ag-AgBr electrode
Gold beater's skin	3.3×10^{-4}	1.12×10^{-4}	6.1×10^{-4}	2.0×10^{-4}	28	29
	4.2×10^{-4}	1.20×10^{-4}	3.9×10^{-4}	8.6×10^{-4}	31	38
	4.8×10^{-4}	1.31×10^{-4}	3.6×10^{-4}	7.2×10^{-4}	33	41
Collodion	3.5×10^{-4}	2.6×10^{-4}	2.3×10^{-4}	1.6×10^{-4}	7.6	9.1
	2.4×10^{-4}	1.7×10^{-4}	2.7×10^{-4}	2.1×10^{-4}	8.1	6.1
	4.0×10^{-4}	2.5×10^{-4}	2.4×10^{-4}	1.54×10^{-4}	11.6	11.5

The equilibrium was also studied under conditions comparable to photographic practice. Plates were bathed with constant rocking in ammonia solutions for three to five minutes, thereby approaching equilibrium within the limits of error of analysis, and the bath analyzed by electrometric titration. In order to eliminate the dissolved silver bromide from the solutions, the ammonia was either neutralized with acid or removed by evaporation; the two methods were found to agree within the limit of reproducibility of either one. The solution was then acidified to pH2–3 to prevent the trace of extracted protein from interfering with the end point, and titrated with 0.001 *N* $AgNO_3$ in the apparatus described in a previous com-

munication (11). Electrometric titration is desirable, as many commercial emulsions contain soluble chloride in amounts as large as 10 molecules to 1 of soluble bromide; we have found the electrometric determination both simpler and more accurate than the possible purely chemical separations, such as the Lang method (13) (14). Figure 1 gives the results for extraction of Seed's 23 plates (emulsion 7,855) with varying concentrations of ammonia. These and subsequent data have been reduced to ratios of soluble bromide to silver bromide in the emulsion; the latter was determined by titration with

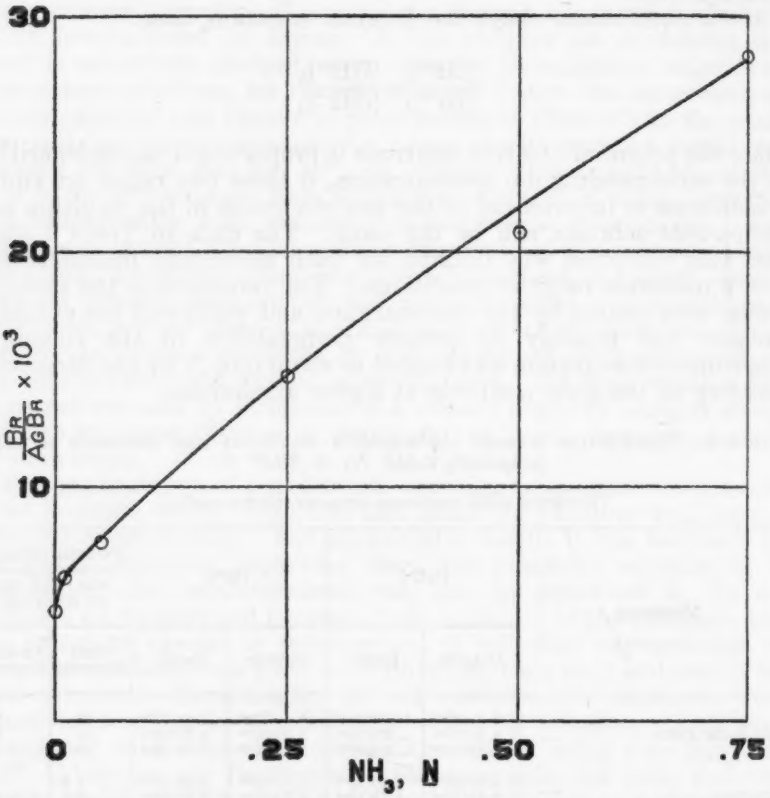


FIGURE 1.—*Soluble bromide removed from Seed's 23 plates by bathing in solutions of ammonia*

Ordinates, ratio of soluble bromide to silver bromide; abscissæ, concentration of ammonia.

cyanide according to the methods of Eggert (15) or Marasco (16). The data in the figure show that approximately 1 per cent of the silver bromide in the emulsion is decomposed by bathing in 0.25 *N* ammonia solution, the quantity increasing with ammonia concentration as would be expected. The existence of the excess silver in bathed plates is readily detected analytically. For example, Seed's 23 plates were given three successive extractions with 0.75 *N* NH_3, the sum of the soluble bromide in the extracts being 2.97 and 3.17 per cent of the total bromide in the emulsion. Nonhalide silver in the emulsion was then determined by cyanide extraction (14) to be 2.30 and 2.38 per

cent of the total silver. The differences, 0.67 and 0.79 per cent are slightly larger than the soluble bromide originally present in the emulsion, 0.47 per cent by water extraction. Similar results were obtained with other emlusions demonstrating that the emulsion is left with an excess of silver over halogen corresponding to the excess of soluble bromide found in the ammonia extract over the soluble bromide originally present in the plate. Analysis of the complete emulsion for total silver and halogen by Clark's method (25) also proved that the soluble bromide found in the ammonia extracts of the Seed's 23 must have come from decomposition of the silver bromide, since no such amounts of soluble bromide were originally present in the emulsion.

The data of Table 1, columns 3 and 4, show that the commercial panchromatic emulsions were left with an excess of 0.2 to 1.0 per cent of silver over halogen after the ammonia treatment which produced the indicated photographic effects. The single extraction with water left the emulsions with a chemically negligible excess of either bromide or silver. As the increase in bromide extracted by the ammonia solution is the result of decomposition of silver bromide in consequence of the membrane equilibrium, the emulsion must have been left with an excess of silver equivalent to the difference between the ammonia and water extracts. It should be noted that the chloride extracted was the same whether water or ammonia was used, indicating that the emulsion closely approached equilibrium with the bath.

Having predicted and established that the result of bathing photographic plates or films with ammonia is to leave them with an excess of silver over halogen, proof of the mechanism of hypersensitization may be completed by comparison of the effects on sensitization produced by ammonia treatment and by addition of soluble silver salts to the emulsion.

III. CORRELATION OF THE CHEMICAL AND SENSITOMETRIC DATA ON HYPERSENSITIZATION

In previous communications (2) (17) we have reported the effects of increasing the silver ion concentrations of emulsions by addition of soluble silver salts before coating. In the absence of sensitizing dyes, there was a slight increase in sensitivity at normal values of pH. Sensitization by dyes was found to be selectively increased by large amounts, so that the most characteristic change was an increase in relative sensitivity for the longer wave lengths. Sufficient increase in silver ion concentration, however, caused a decrease in sensitization by some of the basic dyes, which had been predicted by theoretical consideration of adsorption relations.

Data on the effect of ammonia treatment of emulsions sensitized with known dyes are presented in Table 5. These are representative of a considerable number of experiments; they were selected as far as possible to compare the behavior of different dyes in the same emulsion. It will be observed that in all cases sensitization by pinacyanol was increased by ammonia; this is also true for erythrosin, although the increase in one case was quite small. Sensitization by pinaflavol was decreased by ammonia in every case where the dye was applied by bathing. In one emulsion, 4–103, the sensitivity passed through a maximum with increasing concentration of ammonia,

corresponding to sensitization by pinaflavol with increasing silver ion concentration in the emulsion (2) which also passes through a maximum. This indicates that the failure of many commercial panchromatic emulsions to hypersensitize may be attributed to the characteristics of the dyes which are used. (Table 1.) Results with emulsion 4–128 are an exception; in the other experiments not recorded, hypersensitization of pinaflavol-sensitized emulsions occurred about one time in three. The sensitization by pinaverdol appeared to approach a maximum with increasing ammonia concentration, as would be expected from its behavior with increasing silver ion concentration.

TABLE 5.—*Hypersensitization with known dyes*

[Letters represent commercial emulsions which were bathed in the dye solutions, the ammonia being added to the dye bath. Figures represent experimental emulsions which were sensitized before coating and subsequently bathed with water or ammonia solutions]

Dye	Emulsion	Ammonia concentration N	Speed number for exposure through minus blue filter (compared at constant γ)	Fog for 6 minute development
Pinacyanol	A	0	25	0.40
		.05	59	.63
	4–103	0	13	.09
		.05	20.5	.05
		.25	50	.19
	4–128	0	36	.13
		.25	76	.24
Pinaflavol	A	0	28	.49
		.05	21	.50
	4–103	0	10	.18
		.05	17	.28
		.25	12.5	.39
	4–128	0	10	.65
		.25	23	.72
Erythrosin	B	0	21	.13
		.50	44	.28
	4–103	0	8	.02
		.05	19.5	.02
		.25	24	.04
	4–128	0	27	.15
		.25	29	.24
Pinaverdol	A	0	26	.09
		.05	53	.29
		.25	60	.72

Other amines are capable of producing effects similar to ammonia, by the same mechanism. We have already reported the mild hypersensitizing action of pyridine (18). Extraction of Seed's 23 plates with $N/2$ pyridine solution was found to remove soluble bromide equivalent to 0.66 per cent of the total bromide, indicating that the plate was left with 0.2 to 0.3 per cent excess silver. Triethanolamine has recently (19) been recommended for hypersensitizing. We have tested its action with pinacyanol and pinaverdol, and found that it is photographically equivalent to ammonia of lower concentration. Correspondingly, 0.25 N triethanolamine left a given emulsion with 0.3 per cent excess silver, and 0.25 N ammonia with 0.9 per cent excess. The lower alkalinity of triethanolamine is probably an advantage in cases where there is serious tendency to fog.

Bokinik (20) has recently observed, by comparing plates bathed with water and with dilute silver nitrate solution, that increased silver ion concentration has little effect on sensitivity in the absence of dyes, but produced typical hypersensitization of panchromatic emulsions. He further demonstrated that it was not a development effect. We have also experimented with hypersensitization by bathing in dilute silver nitrate solutions; pinacyanol-sensitized emulsions were hypersensitized, and pinaflavol-sensitized emulsions were slightly decreased in speed, but the results were more difficult to reproduce than when the silver salts were added to the emulsion before coating.

As predicted theoretically, dissolved silver salts in an ammonia bath increase its effect without change in the mechanism; typical examples are given as part of the data in Tables 6 and 7. In general, we have found little advantage in their use, as few emulsions are improved by silver ion concentrations higher than those produced by bathing in 0.5 *N* ammonia. As the membrane equilibrium just discussed would not apply to a collodion emulsion, it would be necessary to add silver salts to the hypersensitizing bath to leave such an emulsion with excess silver.

The increased silver ion concentration produced by ammonia treatment is the principal factor in hypersensitization. However, others have been suggested, and some of these must be considered seriously.

Alkalinity tends to increase sensitization by some of the dyes, notably pinacyanol and erythrosin (2). The effect is not large. One per cent borax solutions (pH 9.2) were carefully compared with pure water as solvent for dyes and for after treatment of emulsions sensitized before coating; the difference was negligible. Of course, if the dye has been applied from an acid bath, as is recommended for kryptocyanine (21) and isocyanines (22), it is desirable to neutralize the remaining acid with some alkaline buffer, such as borax.

Jacobsohn (8) has suggested that treatment with ammonia may break down silver bromide-allyl thiocarbamide complex, thus forming new sensitivity nuclei of silver sulphide. He had originally observed in his extensive experiments on hypersensitization that some emulsions were much more affected by given treatment than others; comparison of otherwise similar emulsions made by the neutral ("boiled") and ammonia processes showed that the former was much better adapted to hypersensitization than the latter. As the neutral type of emulsion might be expected to contain more unchanged complex, he explained the difference between the emulsions on this basis. It is impossible to say that this does not occur, even with the short time and low temperatures of hypersensitization, especially as the reaction is accelerated not only by the ammonia, but by the increased silver ion concentration. The emulsions used for the experiments recorded in Tables 2 and 3 were such that appreciable quantities of unchanged complex might have been present, and the increase in sensitivity of the unsensitized portions on treatment with ammonia indicates that new nuclei may have been formed. However, Jacobsohn's hypothesis is inadequate as a complete explanation of hypersensitization. The experiments by Sheppard (1) on the effect of silver sulphide nuclei on sensitization by dyes, which were quoted by Jacobsohn in support of his hypothesis, show that the relative sensitivity to the longer wave lengths remains

practically constant on the formation of nuclei. Experiments in this laboratory (2) have also indicated that the relative sensitivity is constant, or decreases, whereas an increase in this ratio is characteristic of hypersensitization. The large effects of bathing with pure water are certainly to be explained by extraction of soluble bromide rather than by formation of new nuclei, since no commercially stable emulsion could be appreciably ripened in the short time and low temperature of bathing and drying. The effects of ammonia appear to differ only quantitatively from those of water. No certain explanation of Jacobsohn's observations can be given, since the actual emulsions are not available. However, factors other than unchanged silver bromide-thiocarbamide complex may make neutral emulsions better adapted to hypersensitization than those made by the ammonia process. Their pH is lower, so that more change both in hydrogen and silver ion concentrations would be produced by ammonia treatment. We have observed that under the same washing conditions ammonia process emulsions reach the lower bromide ion concentration, so that this may also reduce the change caused by the ammonia.

It has also been suggested that formation of silver nuclei by reduction of silver bromide might be a cause of hypersensitization. This explanation was used by Schmieschek (23) to account for hypersensitization by mixtures of silver salts and hydrogen peroxide. However, his conclusions are not supported by the experimental evidence. As far as can be determined by study of his publications, Schmieschek compared the plates treated with the mixed solutions only with untreated plates, and thus failed to observe that the hydrogen peroxide contributed nothing to the hypersensitization. His formulas were carefully tested on two emulsions, one of which, the Agfa Special Rapid panchromatic, had been used in his own experiments. The results are recorded in Tables 6 and 7. All the data in each table were obtained from plates which had been bathed under the same conditions of temperature, agitation, and time, dried together, and developed together after exposing. It is evident from the data that the ammonia-silver tungstate-hydrogen peroxide mixture was less satisfactory as a hypersensitizing bath than the ammonia alone, since at the best it produced no greater increase in sensitivity and the fog was higher. The same results were obtained in repeated tests. The peroxide decreased the effect of ammonia, and was of very doubtful advantage to the mixture of ammonia and silver salts, so that we are unable to agree with Schmieschek that it has any significant function. The Agfa plates were also bathed with mixtures of acetic acid, silver sulphate, and hydrogen peroxide as recommended by Schmieschek, and with the acid and silver sulphate, the plates being washed in faintly alkaline tap water after bathing. Both baths caused fog and desensitization, the decrease in sensitivity being greater from the mixture with the peroxide. Bokinik (24) also reports that he was unable to confirm Schmieschek's results, hydrogen peroxide decreasing rather than increasing the effect of silver salts.

TABLE 6.—*Hypersensitization of Agfa Special Rapid panchromatic plates (emulsion Q1666) by combinations of ammonia, silver tungstate, and hydrogen peroxide*

Composition of bath, grams per liter			Speed at $\gamma=1.0$		
Ammonia	Silver tungstate	Hydrogen peroxide	White light	Red light	Fog for 6-minute development
0	0	0	265	18	0.15
.65	0	0	360	38	.23
.65	0	.75	380	29	.28
.65	.14	0	430	31	.41
.65	.14	.75	320	39	.66

TABLE 7.—*Hypersensitization of Wratten "M" plates (emulsion 5173) by combinations of ammonia, silver tungstate, and hydrogen peroxide*

Composition of bath, grams per liter			Speed at $\gamma=1.8$		
Ammonia	Silver tungstate	Hydrogen peroxide	Blue light	Yellow light	Fog for 6-minute development
Untreated plate			10.5	59	0.13
0	0	0	11.5	86	.20
.65	0	0	15.2	180	.33
.65	0	.75	9.2	85	.22
.65	.14	0	9.7	140	.33
.65	.14	.75	13.5	145	.34

Bokinik (24) reports that both panchromatic and unsensitized plates were increased in sensitivity by bathing with 0.1 per cent (0.02 *M*) solutions of hydrazine hydrate. A reference in the summary of his paper indicates that other reducing agents were used, but no others are mentioned in the text. Bokinik's experiments with hydrazine were repeated with a number of commercial and experimental emulsions, some of the data being given in Tables 2 and 3. It was found necessary to use more dilute solutions than his; 0.001 to 0.0015 *M* gave at least as much increase in sensitivity as stronger solutions, and less fog. Commercial unsensitized emulsions such as the Eastman 33 were not increased in sensitivity by either hydrazine or ammonia. The effect of the hydrazine on the unsensitized portions of experimental emulsions 4–143 and 4–145 (Tables 2 and 3) was quite small, so that it is improbable that it produces new sensitivity nuclei of silver. The pinacyanol-sensitized portions of emulsions 4–143 and 4–145 were hypersensitized by the hydrazine, the action being similar to that of ammonia, but considerably less. Similar results were obtained with Eastman infra-red sensitive plates (emulsion 5,875).

The hypersensitizing action of the hydrazine is greater than can be explained by its alkalinity alone. Analysis of 0.0015 *M* hydrazine hydrate solutions which had been used for bathing plates showed that they had extracted practically no more bromide than water, so that the increase in silver ion concentration in the emulsions, compared

to that produced by water, was negligible. Formation of new sensitivity nuclei by reduction of the silver bromide was improbable because the sensitivity to the longer wave lengths was selectively increased. It is possible that the increase in reduction potential of the emulsion can cause a moderate amount of hypersensitization. In order to test this hypothesis without the complications of membrane equilibria introduced by bathing the plates, small amounts of hydrazine and other reducing agents were added to sensitized emulsions just before coating. In this case, however, the reducing agent comes in contact with the warm liquid emulsion followed by a relatively slow drying, and a concentration of reducing agent producing a given potential may cause fog when it would not do so at the low temperature and short drying period used in bathing; for example, hydrazine at five times the maximum concentration given in Table 8 was found to cause heavy fog, although this amount made the liquid emulsion only 0.0010 *M* with respect to the hydrazine. The data are given in Table 8, omitting negative results with sodium arsenite and hydroxylamine hydrochloride. Ammonia is included in this table for comparison with the results obtained by bathing similar emulsions (as 4–145) with ammonia, not because it was considered to have appreciable reduction potential. The increase in sensitivity is about what might be expected from the increase in pH, which amounted to one unit, and is of a lower order of magnitude than the effect of bathing with ammonia solutions with the resulting membrane equilibrium.

TABLE 8.—*Effect of reducing agents on sensitization by dyes*

[Speed numbers are relative values, obtained by exposure through the Wratten filters only, without the Davis-Gibson correction filter; all values for development to $\gamma=1.0$. "B" (green) filter used for erythrosin-sensitized emulsion; "A" (red) filter for pinacyanol-sensitized]

Dye	Reducing agent	Molar ratio, reducing agent to silver halide	Speed through "C" (blue) filter	Speed through "B" or "A" filter	Ratio of speed numbers
Erythrosin	Control	0	125	54	0.44
	Ammonia	1.3×10^{-3}	130	55	.43
	Sodium sulphite	1.3×10^{-3}	155	87	.56
Pinacyanol	Control	0	64	165	2.6
	Ammonia	1.3×10^{-3}	75	215	2.9
	Sodium sulphite	1.3×10^{-3}	75	265	3.5
Pinacyanol	Control	0	37	130	3.5
	Hydrazine	2.8×10^{-4}	43	175	4.0
	Hydrazine	1.1×10^{-3}	53	180	3.4
	p-hydroxyphenylglycine	1.5×10^{-3}	60	170	2.9

The positive results with hydrazine, sodium sulphite and "Glycine" indicate that reducing agents may produce some increase in sensitization by dyes, even though they are without effect on the unsensitized emulsion. Control experiments demonstrated that neither sodium sulphite nor hydrazine added in these quantities and under these conditions increased the sensitivity of similar emulsions in the absence of dyes. This is at least consistent with the simple chemical theory of sensitization which we advocate as the best starting point for a complete theory. If the reduction potential of the emulsion is increased, activation of the dye by light might be expected to

cause more reaction with the silver bromide. It should be understood, however, that in admitting the possibility of hypersensitization by reducing agents, we do not accept this as the explanation of hypersensitization by ammonia or amines, or combinations of ammonia or amines with soluble silver salts. The much greater hypersensitization produced by the latter class of materials is caused by increase in the silver ion concentration of the emulsion, as the result of membrane equilibrium followed by drying with the removal of the ammonia or amine. In this case there has been an increase in the oxidation potential of the silver bromide by adsorption on it of free silver ions, instead of increase in the reduction potential of its environment.

Knowledge of the mechanism of hypersensitization serves to point out the inherent limitations of the process rather than to suggest improvements in procedure. Increase in sensitivity is necessarily gained at the expense of stability; the optimum excess of silver, which may be controlled by the ammonia concentration, depends on the use to be made of the hypersensitized material. In general, the more rapid the drying the higher concentration of ammonia may be used. Addition of alcohol to the bath aids in drying; it decreases the effect of a given concentration of ammonia by decreasing the dissociation, so that it is generally better to use aqueous solutions, followed by soaking the plate in 95 per cent alcohol to accelerate drying. Attempts to improve the stability of bathed plates by adding bromide to the dye bath must necessarily do so at the expense of sensitivity, since the effects of the ammonia and the bromide are opposed to each other. As soluble bromide is shown to accumulate in hypersensitizing baths or dye baths, it is obvious that their effectiveness will rapidly fall off with use, even though the ammonia concentration remains practically the same. Combination of silver salts with ammonia is little different from the use of higher concentrations of ammonia, although it may be preferable if it desired to avoid high alkalinity; difficultly soluble silver salts, such as the chloride or tungstate, are preferable to silver nitrate, since the maximum silver ion concentration which they can produce is limited by their solubility and there is less danger of fog from use of an excess.

IV. ACKNOWLEDGMENTS

C. M. Kretchman has rendered valuable assistance in the sensitometric work, in coating the experimental emulsions, and in some of the bathing experiments.

V. LIST OF REFERENCES

1. Sheppard, Colloid Symposium Monograph, vol. 3, p. 1, 1925.
2. Carroll and Hubbard, B. S. Jour. Research, vol. 9 (RP488), p. 529, 1932.
3. Schumann, Phot. Wochenbl., p. 395, 1885, and p. 49, 1886.
4. Dieterle, vol. 3–3, Sensibilisierung und Desensibilisierung, p. 227.
5. Burka, J. Frank. Inst., vol. 189, p. 25, 1920.
6. Walters and Davis, B. S. Sci. Paper No. 422.
7. Wall, History of Three-Color Photography, p. 222.
8. Jacobsohn, Zeit. f. wiss. Phot., vol. 27, p. 19, 1929, also "Theorie und Praxis der Übersensibilisierung."
9. Carroll and Hubbard, B. S. Jour. Research, vol. 8 (RP430), p. 481, 1932.
10. Donnan, Zeit. f. Elektrochemie, vol. 17, p. 572, 1911.

11. Carroll and Hubbard, B. S. Jour. Research, vol. 7 (RP376), p. 811, 1931.
12. Lüppo-Cramer, Phot. Ind., vol. 14, pp. 78, 111, 1916.
13. Mitchel and Rawling, Proc. 8th Int. Cong. Phot., p. 56, 1932.
14. Carroll and Hubbard, B. S. Jour. Research, vol. 8 (RP447), p. 711, 1932.
15. Eggert, Zeit. f. wiss. Phot., vol. 22, p. 209, 1924.
16. Marasco, Ind. Eng. Chem., vol. 16, p. 945, 1924.
17. Carroll and Hubbard, J. Soc. Motion Picture Eng., vol. 18, p. 600, 1932.
18. Carroll and Hubbard, B. S. Jour. Research, vol. 4 (RP173), p. 693, 1930.
19. Mees, J. Opt. Soc. Am., vol. 21, p. 753, 1931.
20. Bokinik, Zeit. f. wiss. Phot., vol. 30, p. 322, 1932.
21. Dundon, Am. Phot., vol. 20, p. 670, 1926.
22. Von Hübl, Koll. Zeit., vol. 27, p. 263, 1920.
23. Schmieschek, Phot. Ind., vol. 28, pp. 445, 472, 1930.
24. Bokinik, Zeit. f. wiss. Phot., vol. 30, p. 330, 1932.
25. W. Clark, J. Chem. Soc., p. 749, 1925.

WASHINGTON, November 23, 1932.

TEMPERATURE EFFECT AND ITS ELIMINATION IN GEIGER-MÜLLER TUBE COUNTERS

By L. F. Curtiss

ABSTRACT

It has been found that in the usual form of the Geiger-Müller tube counter the rate of counting is affected by changes of temperature. The rate of counting, at a fixed potential applied to the tube, decreases as the temperature is increased. This indicates an increase in the density of the gas in the counter. Since it is hermetically sealed this can only be caused by evaporation of volatile material within the counter. The hard-rubber insulators commonly used in these counters are practically the sole source of such volatile material, consequently a form of counter has been devised in which only glass and metal are used and which does not have its rate of counting affected by changes of temperature.

CONTENTS

		Page
I.	Introduction	229
II.	Effect of temperature on usual form of counter	229
III.	Description of improved counter	231
IV.	Effect of temperature on improved counter	231
V.	Acknowledgments	232

I. INTRODUCTION

In the course of a study [1] of the magnetic deviation of cosmic-ray particles, using Geiger-Müller tube counters, it was found that changes in the temperature of the counters affected their rate of counting. This effect may lead to erroneous results in experiments where precautions are not taken to maintain the temperature of the counters constant. The increasing use of these counters makes it desirable to have some knowledge of the cause of this behavior. Since it is frequently necessary to operate counters continuously over periods of several days, the elimination of this characteristic would greatly simplify the apparatus required if reliable results are to be obtained. This problem has been investigated and a form of counter devised which does not show a systematic change in rate of counting with changes of temperature.

II. EFFECT OF TEMPERATURE ON THE USUAL FORM OF COUNTER

The usual form of the Geiger-Müller tube counter consists of a metal tube with a wire stretched along its axis. This wire is supported at each end by insulating bushings fitted to the ends of the tube. The tube is exhausted to a pressure of a few centimeters of mercury, and

[1] B. S. Jour. Research, vol. 9 (RP509), p. 815, 1932.

sealed. A high degree of insulation is not required, hence hard rubber is commonly used for these bushings.

Nearly all counters constructed as outlined above have been found to show a marked decrease in rate of counting when their temperature is raised. Although in some cases this variation was not sufficient to be detected when the temperature changed only a few degrees, more frequently even small changes produced a noticeable effect. In these cases an increase of about 15° caused the counter to cease to function entirely. Almost without exception the original counting rate was observed on bringing the counter back to the original temperature.

An example of the change of the rate of counting with temperature for counters of this design is shown in Figure 1. The rate of counting is plotted against the temperature, the points indicated by open circles referring to the type of counter under discussion. In obtaining

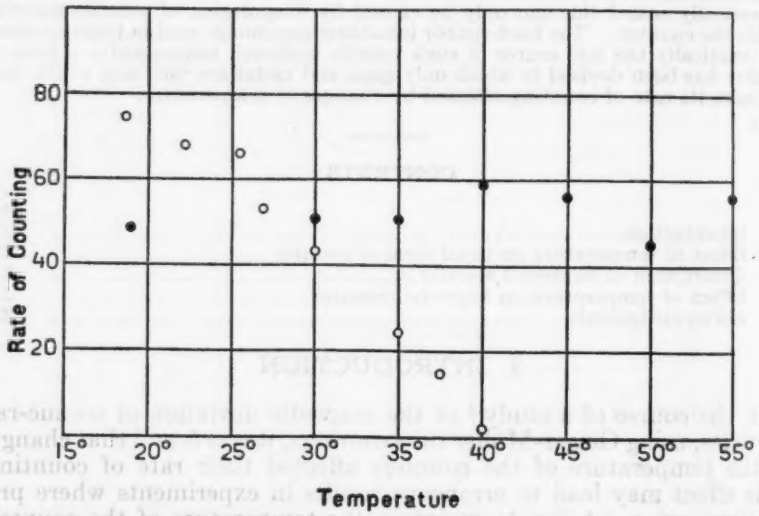


FIGURE 1.—*Graphical representation of the effect of changes of temperature on the average rate of counting of Geiger-Müller tube counters*

○, previous form of counter with hard-rubber bushings.
●, improved form made entirely of glass and metal.

these data, care was taken to maintain the voltage applied to the tube constant to within one-half of 1 per cent. As the graph reveals, this counter, which was counting at an average rate of about 70 per minute at 19°, ceased to count entirely at 40°. The variation of even a few degrees in the neighborhood of 20° had an observable effect on its rate.

This is what is to be expected if the pressure in the counter had been increased by permitting additional air to enter, thus increasing the density of the air in the counter. In the case of a sealed counter, however, no additional air can enter. The natural explanation for this increase in density is that volatile material is present in the counter. The only apparent source of this material is the insulating bushings. Accordingly, a form of counter was constructed in which only glass and metal were used.

III. DESCRIPTION OF IMPROVED COUNTER

To avoid the use of a metal tube which might be contaminated with volatile substances, a copper tube was out-gassed in a vacuum furnace and used for the tubular part of the counter. Metal bushings were soldered into the ends of the copper tube to support pyrex-copper seals, *CC*, as shown in Figure 2, which represents a cross section of a completed counter. To shield the central wire from the adjacent metal parts at the ends, glass sleeves, *GG*, were sealed in as shown. They insure that electrical discharges occur only in the main volume of the counter. In assembling the counter, the wire with tungsten lead attached was inserted at the end, *S*, while still open, and the tungsten lead was sealed in at *T*, sufficient tension being put on the spring inside the sleeve at the opposite end to make certain that the wire will remain taut. The counter was attached to a pump, evacuated to the desired pressure, and then permanently sealed by closing the pyrex tube at *S* by means of a flame. This makes a more rugged counter than the former glass-inclosed types. It is particularly easy to arrange these counters in line for coincidence counting since the tubular part of the counter is directly visible.

FIGURE 2.—*Cross section of improved counter*

IV. EFFECT OF TEMPERATURE ON IMPROVED COUNTER

If the hypothesis is correct that the change in counting rate observed in the earlier type of counters with changes in temperature is caused by vapors from the insulating material, the improved form should not show this effect. The rate of counting of one of these glass-metal counters was observed at various temperatures to see whether the variation had been eliminated.

A counter, constructed as described above and filled with dried air, was used in this test. It was operated at a constant voltage and the temperature was changed by steps of a few degrees. The results are represented in the graph in Figure 1 by the solid dots. Although there is some variation in the rate due to statistical fluctuations—each dot represents a 5-minute average—it is clear that there is no effect of temperature up to 55°. This is a greater range of temperature than is usually encountered in the use of the counter. It is quite safe to assume, therefore, that, for fluctuations of several degrees in the neighborhood of room temperature, there is no change in the counting rate attributable to changes in temperature. This feature is of considerable advantage in experiments in which automatic registration is carried on over long periods of time. Under such conditions it is impossible to maintain counters at a constant tem-

perature without some form of thermostatic control which often introduces troublesome complications.

V. ACKNOWLEDGMENTS

The writer wishes to thank L. L. Stockman and B. W. Brown for help in constructing and testing various designs of counters.

WASHINGTON, December 8, 1932.

OPERATION OF THICK-WALLED X-RAY TUBES ON RECTIFIED POTENTIALS[1]

By Lauriston S. Taylor and C. F. Stoneburner

ABSTRACT

It is found that thick-walled glass, deep-therapy X-ray tubes do not reach a steady state within the first few minutes of operation on some types of generator. All thin-walled tubes tried thus far quickly reach a steady operation state. Depending upon the mode of control of the generator, the X-ray emission of a thick tube may increase or decrease by 10 to 20 per cent on mechanical or valve tube rectifiers and not reach a steady state until some 10 minutes after starting. The change in X-ray emission between the second and tenth minute of operation appears to depend upon the electrical regulation of the transformer. Cooling of the tube walls with strong air blasts delays the attainment of the steady state, but does not affect the magnitude of the net change in emission. For some generators the output remains steady if the effective tube current and voltage be maintained constant. A qualitative explanation of the effect is based on the blocking action of the high negative charge on the glass walls when the tube is cold. As the tube warms up this charge is dissipated through the increased electrical conductivity of the glass. The influence of the effect upon dosage measurements is discussed. The effect is absent when the tube is operated on nearly constant potential.

CONTENTS

	Page
I. Introduction	233
II. Apparatus	234
III. Experimental results	240
1. Variation of X-ray output	240
2. Effect of cooling the tube walls	241
3. Voltage and current variations	242
IV. Discussion	245
V. Effect on "dosage" measurements	247

I. INTRODUCTION

Until recently deep-therapy X-ray tubes of the glass-bulb type have been of soda or other soft glass, with bulbs less than 1 mm in thickness. These tubes were generally satisfactory unless placed in too restricting an inclosure, such as the smaller of the conventional "tube drums."[2]

Within the last two years a tube of Pyrex glass having walls 5 to 7 mm thick has largely replaced the common glass tubes. The pyrex tubes have several obvious advantages; for example, much higher baking temperatures can be used, with consequent improved outgassing in their manufacture. Another feature of the thick wall is the smaller likelihood of its puncture. Where a strong negative charge is built up on the inner wall the potential difference between it and the anode may rise to a point where spark over occurs through air from

[1] Presented at the annual meeting of the American Röentgen Ray Society, Detroit, September, 1932.

[2] Some qualitative experiments in this laboratory (L. S. Taylor and K. L. Tucker, B. S. Jour. Research, vol. 9 (RP475), p. 333, 1932) have shown that for satisfactorily steady operation of a thin-walled tube in such a protective inclosure, there must be a minimum spacing of about 12 to 14 inches between the bulb and any grounded metal parts.

the bulb wall to the anode lead, possibly puncturing the bulb. Sometimes without actual spark over, sufficient current may pass through the bulb at some point to cause local heating of the glass, with consequent release of gas, and a lowering of the vacuum. Thick glass walls would tend to eliminate either of these effects.

Probably most important, and unfortunately not entirely advantageous from an operation standpoint, is the influence of the thick-walled bulb upon the space charge distribution within the tube. In normal operation the inner walls of an X-ray tube acquire a strong negative charge through electrons scattered from the target or lost directly from the cathode stream. This accumulated charge reduces the field intensity at the electron source and for a given applied potential must correspondingly increase it toward the anode, resulting in a "focusing effect" of the cathode beam. This also changes the operating characteristics of the tube, in that higher potentials may be required to produce a given instantaneous electron current. With thin-walled tubes an appreciable amount of local leakage from the inner to the outer surface causes a shifting field and a varying X-ray output. For steady action of the tube it is necessary that this wall charge be either largely eliminated or made very steady. Its influence is not detrimental to the use of the tube but must be taken into consideration, with tubes operated in the usual manner.

In using several thick glass tubes it was noted that while eventually their output became extremely steady, this condition was not reached until several minutes after starting. As this delay in reaching steady operation might have a serious influence upon dosage measurements it became important to investigate the cause of the lag. In this connection we were interested too in the relationship between the effective voltage applied to the tube and the X-ray output.

II. APPARATUS

We have investigated the operation of three thick-walled X-ray tubes of different manufacture and two thin-walled tubes on six different generators: a constant potential (0.2 per cent ripple per milliampere, B. S. Standard),[3] a "constant potential" (2 per cent ripple per milliampere, commercial), a cross-arm mechanical rectifier a double-disk mechanical rectifier, a half-wave valve-tube rectifier, and a full-wave valve-tube rectifier.

To eliminate uncertain variables, each generator as used was connected to the same aerial system, meters, controls, etc.; and the several tubes successively operated in the same container—a lead-covered box 4 by 4 by 7 feet. For cooling purposes the exhausts from two pressure blowers were directed at specified times on the bulb of the X-ray tube as indicated in Figure 1. To insure proper direction of these air blasts, the air was conducted in two 2½-inch rubber tubes to within about an inch of the bulb.

Fine adjustment of the generator voltage was made by means of resistance in the transformer primary circuit after the autotransformer in the same circuit had been adjusted to a 1:1 ratio—this being the most common method of control used in practice. Peak voltages were measured with a sphere gap, which naturally interrupted the operation of the set, but was found to have no influence on the continuity

[3] L. S. Taylor, B. S. Jour. Research, vol. 2 (RP56) p. 771, 1928.

of the other measurements provided the voltage was thrown on again quickly. Average and effective (r. m. s.) high-tension voltages were measured with d. c. and a. c. meters (K_2 and K_1), respectively, in series with a 150-megohm corona-shielded resistor R;[4,5] average and effective tube currents were measured with d. c. and a. c. milliammeters (M_2 and M_1) in the high-tension circuit. A Leeds & Northrup potentiometer recorder was shunted around a resistance r_3 in series with the 150-megohm resistor as shown. This, for the voltage range used, had a sensitivity of about 350 volts per division at the 150,000 volts(average) applied across the tube. Use of the recorder simplified the process

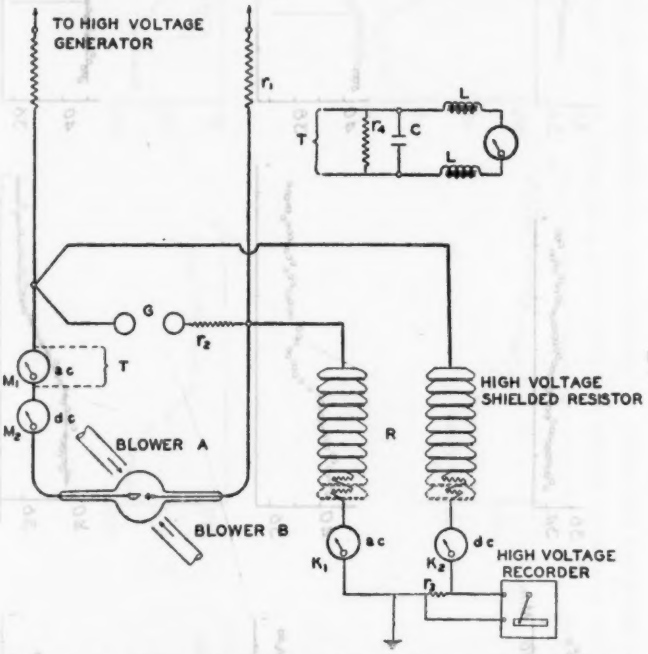


FIGURE 1.—*Schematic diagram of X-ray tube and apparatus for measuring currents and voltages*

Inset *T* shows filter circuit always used in conjunction with the thermomilliammeter for measuring r. m. s. tube current. *A* and *B*, blowers for cooling tube.

of making observations and also provided a very accurate record as to steadiness of the tube-operating potential.

Suitable oscillograph facilities not being readily available, voltage and current wave form changes were obtained qualitatively from other measurements with sufficient accuracy for our purposes.

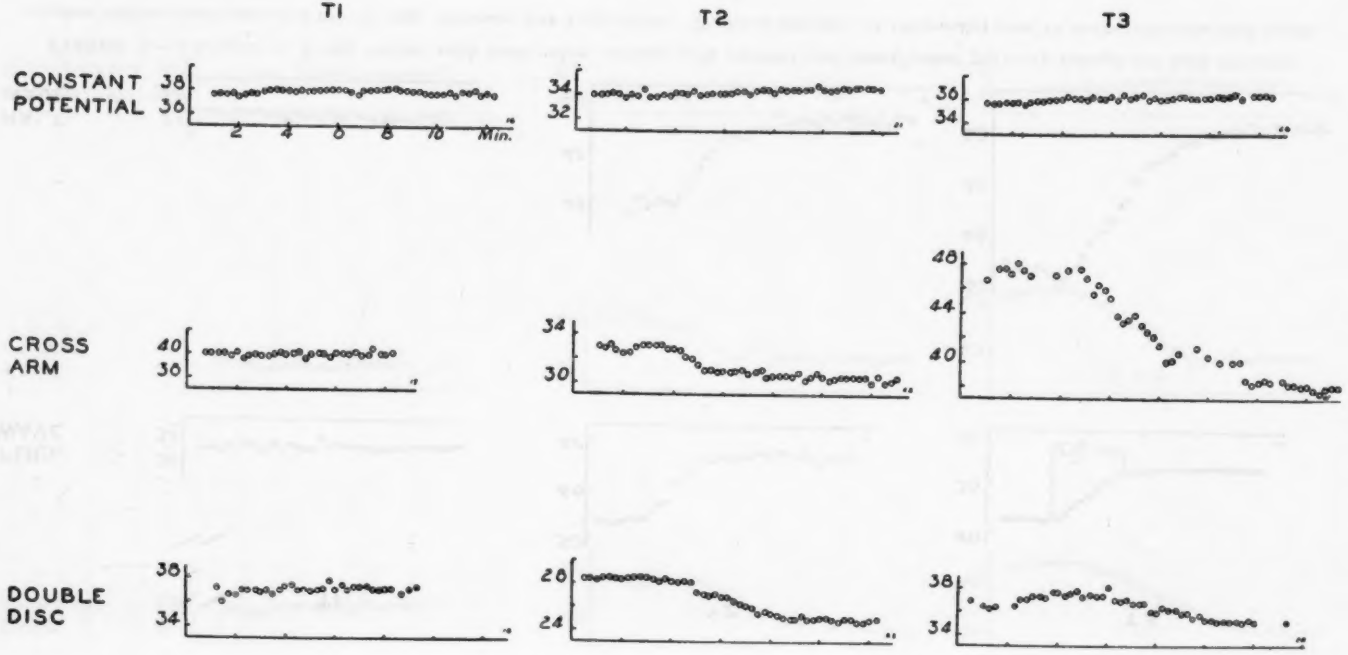
The tube output was measured in terms of air ionization with a multiplate ionization chamber consisting of 11 thin aluminum plates spaced about 1 cm apart.[6] In this, one set of alternate plates was connected to a 400-volt saturation source and the other set to earth through a galvanometer, of such sensitivity that a working deflection of 40 to 50 cm was always obtainable.

[4] L. S. Taylor, B. S. Jour. Research, vol. 5 (RP217), p. 609, 1930.
[5] L. S. Taylor, G. Singer, and C. F. Stoneburner, B. S. Jour. Research, vol. 9 (RP491), p. 561, 1932.
[6] J. L. Weatherwax "Physics of Radiology," p. 140, Paul Hoeber ,1931.

T1
T2
T3
CONSTANT POTENTIAL
CROSS ARM
DOUBLE DISC
36
34
38
40
Min.
2
4
6
8
10
4½ min
6 min

FIGURE 2.—*Changes in X-ray output with time, when average tube current and transformer primary voltage are held constant*

Abscissæ divisions show intervals of two minutes. Ordinates show X-ray output. *T1*, thin-walled tube; *T2*, thick-walled tube; *T3*, thick-walled tube (disk target).


T1
T2
T3
CONSTANT POTENTIAL
38
36
2
4
6
8
10
Min.
34
32
36
34
CROSS ARM
40
36
34
30
48
44
40
DOUBLE DISC
38
34
28
24
38
34

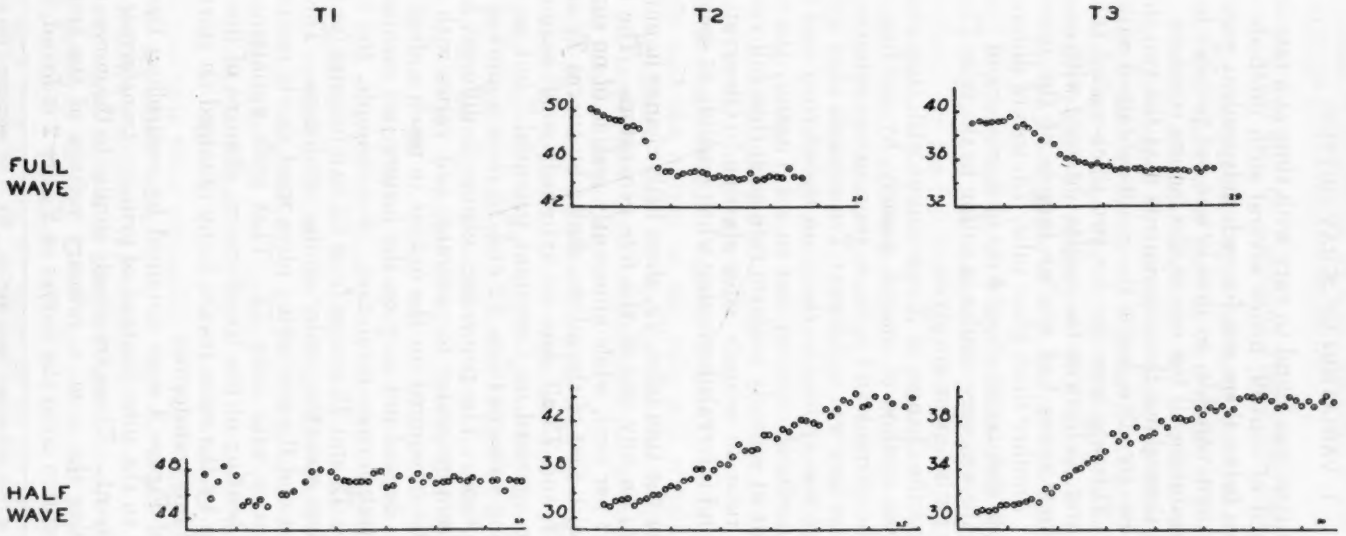


FIGURE 3.—*Changes in X-ray output with time when average tube current and average tube voltage are held constant*

Abscissæ divisions show intervals of two minutes. Ordinates show X-ray output. *T1*, thin-walled tube; *T2*, thick-walled tube; *T3*, thick-walled tube (disk target).

III. EXPERIMENTAL RESULTS

1. VARIATION OF X-RAY OUTPUT

The X-ray output was found to vary with time at a rate dependent upon the method of control, hence several such methods were employed. As seen below there was for each independent variable more than one dependent variable, so that it was not possible in any one experiment to maintain all but one of the factors constant.

It was found throughout the experiments that the two thin-walled tubes behaved exactly alike, hence the results obtained with but one, *T1*, are given. This was true also for two thick-walled tubes of the same manufacturer, so likewise the results obtained with one, *T2*, are given. These four tubes had similar targets of the massive solid tungsten type. Another thick glass tube, *T3*, was of different make, having a tungsten disk target about 6 cm in diameter and 1 mm thick. Although this tube was very similar in action to the tube *T2*, separate curves showing its behavior are given.

Figure 2 shows the changes in X-ray output with time obtained by the more common method of control, namely, by holding constant the average tube current and r. m. s. transformer primary voltage. The general procedure was as follows: Ten seconds after lighting the filament, voltage was applied to the main transformer and the auto-transformer immediately cut out (set to a 1:1 ratio); the resistance was then cut out at a nearly uniform rate such that full voltage was applied to the tube 30 seconds after starting.[7] Observations were made at 15-second intervals beginning when possible 45 seconds after starting.

The curves for the thin tube, *T1*, show little change in output with duration of run, on any one of the five generators. The observed change of 1 to 2 per cent, while apparently real, is of no significance in comparison with that of the others, shown by curves *T2* and *T3*.

Tubes *T1*, *T2*, and *T3* all show an extremely small output change with time when operated on "constant potential," but on rectifiers yielding pulsating voltages tubes *T2* and *T3* show a marked decrease in output with time. The percentage change is different here from tube to tube, from generator to generator and varies with the tube current. The time required for the output to reach a steady magnitude appears to depend not only on the factors just mentioned, but also upon the transformer regulation. For example, the transition period for curves *T2* and *T3* ranges from 2¾ to 6 minutes for the three full-wave rectifiers operating under similar conditions. The greatest change in output and the one taking place most slowly occurs for the half-wave generator with tube *T3*. That such variations are not attributable to heating of the transformers, changes of line voltage, etc., was proven by the same results being obtained on starting with a cold tube and hot transformer.

The curves of Figure 3 were obtained by controlling the average voltage applied to the tube (instead of primary transformer voltage) and the tube current. These are closely similar to the curves obtained by simply holding the r. m. s. primary voltage of the transformer constant. Exception from the curves in Figure 2 is found, however,

[7] The entire tube was at room temperature before starting. We do not recommend this fast starting of cold tubes in general practice. Those tubes used here had all been carefully tested relative to their ability to stand such treatment.

for the half-wave generator where the output increases some 25 per cent instead of decreasing by a like amount, when the transformer primary voltage is maintained constant.

2. EFFECT OF COOLING THE TUBE WALLS

In all of the observations thus far mentioned, the X-ray tube was started cold and allowed to heat up as a result of the power input of the tube without artificial cooling. If, however, with transformer primary voltage control, a strong air blast be directed on the tube bulb behind the face of the target (blower *A* in fig. 1) the output falls off very slowly with time (fig. 4, *A*) requiring some 12 minutes to reach a steady state, as compared with about 5 minutes without cooling. This may be compared with the curve for tube *T3* operating on the cross-arm rectifier.

Figure 4, *B*, shows that an air blast, such as from blower *B*, directed on the part of the tube bulb facing the target has a much more pronounced effect. In the full line curve the output falls off very slowly up to the point *a* where the blower is turned off, following which it falls off in the usual manner as compared with the normal curve. If, after a few minutes' operation without blower, this is again started, at *b* on the time curve, the output begins at once to rise toward the point *c* where turning off the blower leads in another decline. This operation was carried out in a variety of ways with always the same result. With both blowers of Figure 1 operating the output fell off only 2 or 3 per cent in 30 minutes.

It is to be concluded that so long as the X-ray tube is maintained sufficiently cool the output of the tube will remain constant with constant input, and that by cooling the hemisphere of the bulb opposite the target face the steadying effect is greater than by cooling applied behind the target.

This result suggested that by changing the power input of the tube, the bulb would be heated at a different rate and that there would be a consequent alteration in rate of change of the X-ray output. The obvious way of testing this was to change the tube current. However, because of the fact that most X-ray transformers have very poor electrical regulation, a change in tube current also changes the wave form so seriously as to mask any quantitative relation between current input at a definite potential and X-ray output. Attempts to study this change in heating on the two mechanical rectifiers were unsuccessful. Most of the runs up to this time had been made with a tube current of 5 ma, the average kilovoltage or transformer primary voltage being adjusted so as to put approximately 200 kv (peak) on the tube. If then keeping the average voltage constant the tube current be raised only 2 ma the resultant peak voltage due to distortion of the wave form reaches a dangerously high value. The same was true when regulating by transformer primary voltage. Since it is obviously impossible to control continuously the peak voltage on such a generator, other methods of control had to be sought.

Change of wave form with load was not as great in the case of the full-wave kenetron rectifier as for the mechanical rectifiers, although it was still present. The three curves in Figure 4, *C*, show the change in output with time of tube *T3*, operated on the full-wave generator, as the tube current is increased. In this the average kilovoltage was kept constant during the run. A change of current from 4 to 5 ma

changed the drop in output from 3 to 11 per cent. The corresponding final peak voltage increased from 192 to 196 kv. Changing the tube current to 6 ma, the peak voltage exceeded 200 kv so that the average voltage was dropped from 157.5 to 150 kv (average). The drop in output nevertheless increased to 18 per cent, though the lower operating voltage may have masked the true change in this case.

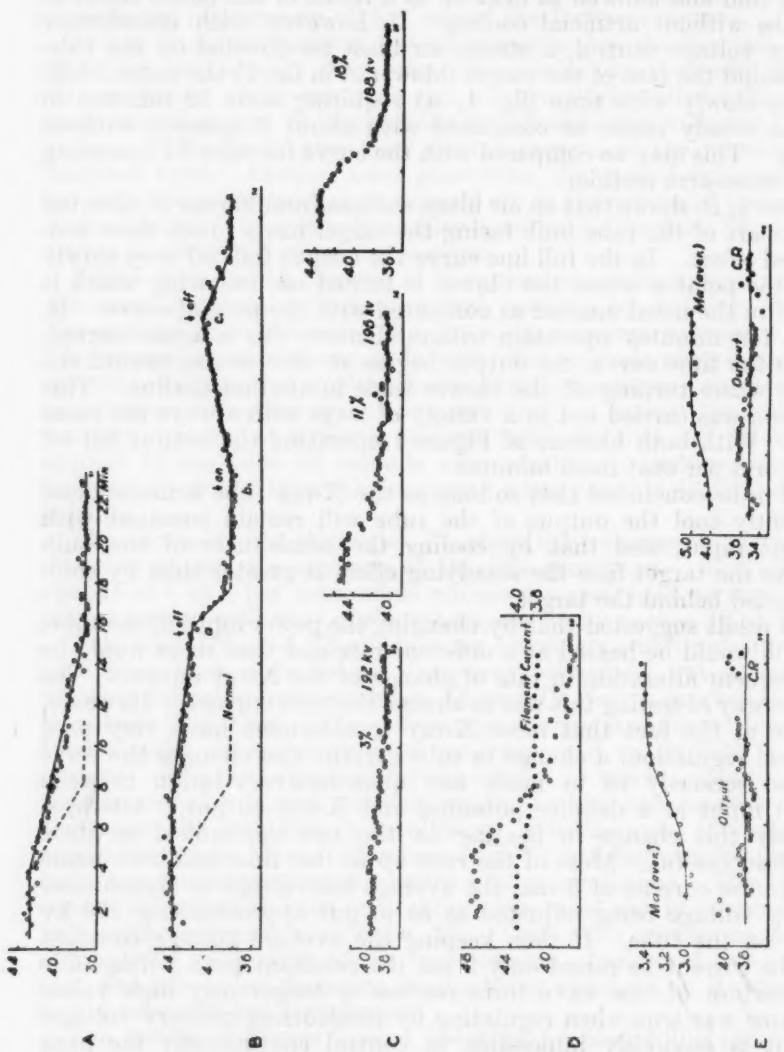


FIGURE 4

Abscissa divisions show intervals of two minutes. Ordinates show X-ray output. Curves *A* and *B*, mechanical rectifier, average tube current and voltage held constant. Curves *C*, full-wave rectifier at 4, 6, and 6 ma (average), average voltage held constant. Curve *D*, mechanical rectifier, average tube current and voltage held constant. Curves *E*, half-wave and full-wave generators with effective tube current and voltage held constant.

3. VOLTAGE AND CURRENT VARIATIONS

Peak voltages given with the curves were in all cases measured at the end of the run, after the tube had reached its steady state. It was noted, however, that if the average tube voltage or transformer primary voltage was maintained constant through a run, the peak voltage of some generators increased from a low initial value to a

much higher final value as the tube changed in output. Figure 5 gives a group of average voltage recorder traces, from which it is found that the average voltage tended to increase along with change in tube output when the transformer primary voltage was held constant. These curves also indicate the degree of steadiness of the tube operation in these studies.

Curves *A*, Figure 6, show the variation with time of peak voltage and tube output in the case of tube *T3* on the half-wave generator operating at 84 kv (average). The output increased 17 per cent in about 10 minutes while the peak voltage increased from 133 to 173 kv, or 30 per cent. Along with this it is found that to maintain the average tube voltage constant the transformer primary voltage was increased some 12 per cent.

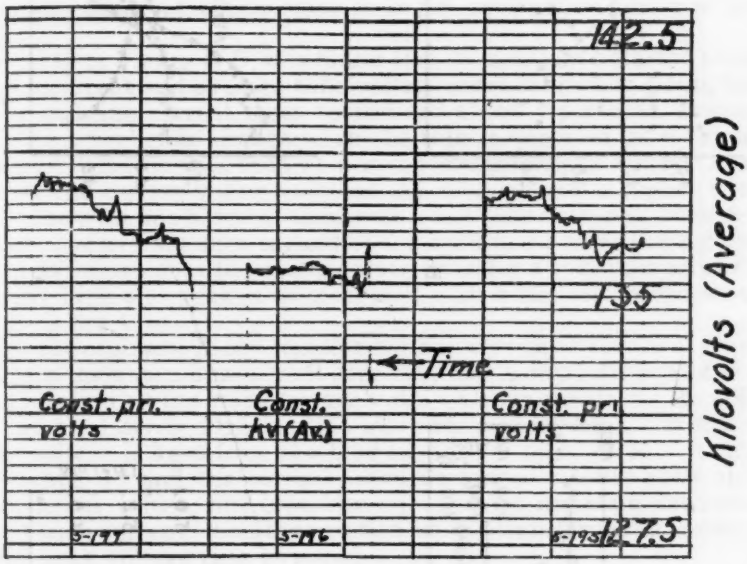


FIGURE 5.—*Traces of average tube voltage obtained with potentiometer recorder*

Time reads right to left.

On the other hand, as shown in Figure 6, *B*, if the transformer primary voltage is maintained constant, the tube output decreases about 22 per cent, the kilovoltage peak increases 26 per cent, the effective tube current decreases 28 per cent and the average kilovolts decrease 19 per cent.

In the case of the full-wave kenetron generator, Figure 6, *C*, in which the average tube current and average voltage were maintained constant, the peak voltage, effective voltage, and primary voltage also remained practically constant, while the tube output fell off with time about 11 per cent and the effective tube current also fell off about 11 per cent. In both cases above (fig. 6, *B* and *C*) the filament lighting current fell off 3 to 4 per cent.

Figure 6, *D*, shows another series of variations which are found with the double-disk mechanical rectifier. As the tube output decreases with time 22 per cent, the effective tube current decreases 22 per cent,

FIGURE 6

Abscissa divisions show intervals of two minutes. Ordinates show X-ray output. Curve *A*, half wave generator with average tube current and voltage held constant. Curve *B*, half wave generator with primary voltage held constant. *C*, full wave generator with average tube current and voltage held constant. Curve *D*, double disk generator with average tube current and voltage held constant.

[1] H.

nd the peak voltage increases about 6 per cent. The transformer rimary voltage decreases only very slightly during this time and the lovolts effective remain constant.

The relative variation of the several factors just shown depends rgely upon the electrical regulation of the transformers and probably hanges from generator to generator. In the case of a power transrmer having excellent regulation the voltage variations will undoubtly disappear.

IV. DISCUSSION

As already pointed out we were primarily interested in this variaion in tube output because of its bearing on dosage measurements nd also because of the possibility that means might be found for its limination. Accordingly we will not go into a detailed discussion of he various observed effects since their full explanation becomes too nvolved.

Referring to Figure 4, *D*, it is found that to maintain both the averge tube current and average tube voltage constant during a run, the lament lighting current must be reduced about 4 per cent, as contrasted to a negligible change when the tube is operated on constant otential. This implies that at a given instantaneous voltage near he crest the corresponding value of the tube current is higher with cold tube with hot filament than with a hot tube with cold filament. But since the average tube current over a cycle is the same throughout he run, it follows that the current wave form for a cold tube must be elatively high and peaked as compared with a low and broad wave orm for a hot tube.

Since the ordinary X-ray transformer has very poor electrical regulation, the instantaneous current drawn by the X-ray tube produces a strong reaction on the voltage wave form. Consequently, as the cold tube has a relatively high current wave for a short time, the transformer voltage is kept from reaching its normal peak value. As the tube warms up and the current wave no longer reaches such high instantaneous values, but broadens out so as to maintain the same average tube current, then the reaction on the transformer is lessened and the peak voltage rises as noted.

Figure 4, *E*, shows that the existence of a high narrow tube current wave with a cold tube is likewise borne out by the fact that when maintaining the r. m. s. tube current and r. m. s. tube voltage constant during a run, the average tube current increases continuously during the time that the tube is warming up. Similarly, Figure 6, *B*, *C*, and *D*, show that when the average tube current and voltage are maintained constant, the effective tube current decreases.

To find a cause for the change in tube current wave form we can assume that within the first half minute or less after applying voltage to the tube, the walls are charged by the scattered electrons to their maximum potential. It has been shown that if the walls of an X-ray tube be allowed to charge freely they will reach a potential very nearly that of the cathode.[8] Under such a condition the presence of this high potential sheath will exert such a strong blocking action between cathode and anode as to require much higher tube potentials to yield a given tube current. Thus in applying a pulsating voltage

[8] H. M. Terrill and C. T. Ulrey, X-ray Technology, D. Van Nostrand, 1930.

to the tube very little tube current will pass until the voltage rises above the point where the space charge in the tube can be overcome. This action will produce a peaked current wave with the consequent effect on the voltage wave form indicated above.

As the tube warms up, the increased glass conductivity dissipates the charge on the inner walls, and the high space charge is gradually reduced to a minimum, whereupon a steady state of operation will be attained. For a given tube and generator, the temperature of the glass appears to be the chief controlling factor as suggested by the curves in Figure 4, *B*. In obtaining these curves measurements of peak voltage made simultaneously with the output measurements showed that for any given value of the output the peak voltage was the same.

When operating with a "constant potential" applied to the tube the same wall charge probably accumulates, but in that case the operating tube potential remains throughout the cycle above the point necessary to overcome the large space charge and hence supplies a constant and normal tube current. Also since the tube is operating above this point there is no change in output as the tube warms with consequent dissipation of the wall charge. Likewise since "constant potential" has little or no ripple there is no cyclic change in the reaction on the generator.

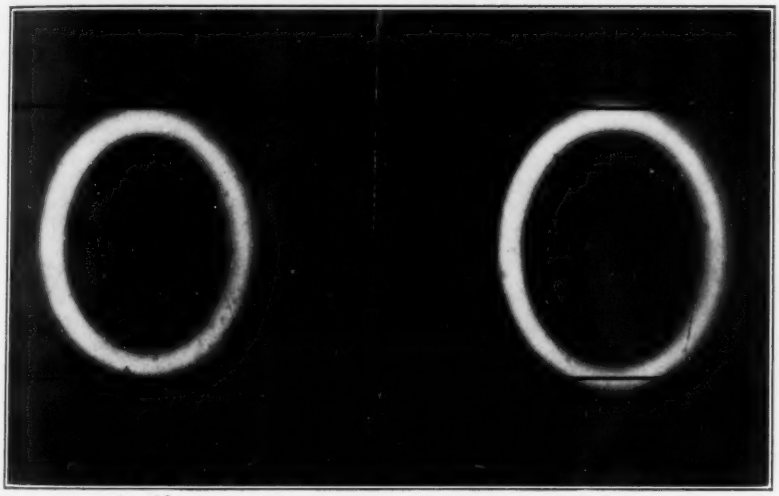
The presence of a high wall charge on a cold tube and low wall charge on a hot tube is demonstrated by the change in the size of the focal spot under these conditions. Pinhole photographs of the focal spot taken during the second two and during the last two minutes of tube operation are shown in Figure 7, *A* and *B*, respectively. It is seen that there is a definite enlargement of the focal ring when the tube is warmed. This is typical for all generators as may be expected.

In all of the output curves shown thus far the factors controlled were average tube current, average tube voltage, or r. m. s. primary voltage. As pointed out above, while these quantities were alternately maintained constant, the effective tube current and voltage and the peak voltage changed. However, as shown by Figure 4, *E*, it was found for the half and full wave kenetron generators that if the effective tube current and effective voltage were held constant that no very great change occurred in the tube output as the tube warmed. Plotted above these are curves showing the rise in average tube current occurring during the normal transition period.

In the case of one mechanical rectifier the output did not remain constant, but increased with time as contrasted with a decrease obtained by using the other methods of control.

To compare the outputs of the pulsating voltage generators with the output on constant potential, the same tube was operated on constant potential at the same effective tube current and voltage as for the half and full wave generators in Figure 4, *E*. The black dots (C. P.) represent the constant potential output under these same conditions of tube current and voltage, from which it is seen that the outputs are very nearly the same. This is in accordance with the results of an earlier investigation [9] where it was found that the outputs of all generators used in conjunction with thin walled therapy tubes were approximately alike for a given effective tube current and

[9] L. S. Taylor and K. L. Tucker, B. S. Jour. Research, vol. 9 (RP475), p. 333, 1932. L. S. Taylor, G. Singer, and C. F. Stoneburner, B. S. Jour. Research, vol. 9 (RP491), p. 561, 1932.



A, cold B, hot

FIGURE 7.—*Pinhole photographs showing variation in size of focal spot as X-ray tube warms*

UNIV. OF MICH.

voltage. This can not be generalized for all generators since, as pointed out above, similar control of the double disk rectifier did not keep a constant X-ray output.

V. EFFECT ON "DOSAGE" MEASUREMENTS

The bearing of this tube effect upon dosage measurements is fairly obvious and need not be dealt with at length.

Since the voltage is usually varying during the transition period, it is clear that the X-ray quality must also be changing. This can be remedied only by constant adjustment to keep the voltage constant. Peak voltage can not be kept constant by any simple means since the frequent operation of a sphere gap interferes with the normal operation of the equipment. However as shown by Figure 4, *E*, control of effective tube current and voltage with some generators appears to eliminate the tube effect while with others it reduces the effect somewhat.

Control of output can be effected only by means of a continuously indicating ionization chamber of some type, which, however, need not read in Röntgens. Instruments of the general type used in this paper are readily available and are in somewhat general use.

Where the X-ray output of a machine is calibrated by means of a dosage meter, measurements made during the first few minutes of tube operation may be very misleading. Depending upon the generator, these calibrations may be too high or too low, thus resulting in under or over treatment, respectively.

It should be recalled that adequate cooling [10] of the tube eliminates the change in output effect. This means that a tube having a normally falling output, if properly cooled may be operated at a higher output than otherwise possible. On the other hand, with a tube having a normally increasing output it is better to permit the tube to warm up thereby yielding a greater output at a given voltage.

In practice, the operating characteristics of the tube should be carefully determined and the "dosage" measurement procedure governed accordingly. The effect is of course absent in water cooled tubes.

This investigation has been made possible through the cordial cooperation of the American X-ray equipment manufacturers. We wish to express our indebtedness to George Singer, of this laboratory, for his assistance in carrying out many of the observations.

WASHINGTON, November 20, 1932.

[10] The customary cooling by blowing air in one end or top of the tube container is inadequate for th elimination of this effect. The air must be applied directly to the tube walls.

APPARATUS FOR COMPARISON OF LENGTH OF GAGES

By Charles Moon

ABSTRACT

Apparatus has been built for comparing spherical-ended gages of quartz having very small thermal expansion with standard flat-ended gages of steel which have a relatively large coefficient of expansion. The difference in length of two gages is measured by a micrometer screw which is driven by a very small reversible electric motor. Screw settings are made automatically by means of an electrical contact indicator which disengages an electromagnetic clutch at a definite measuring pressure. The gage-holding device is made so that the alignment between the measuring faces can be accomplished with the operator at a distance. Hence, the whole operation of length comparison can be made in an inclosed space where the temperature can be accurately controlled.

The gages are supported on steel balls which allow the easy endwise motion necessary when using light measuring pressures.

The sensitivity of the indicator is such that settings are repeated to within 0.1 μ or 1 part in 1,000,000 on gages 10 cm long.

CONTENTS

	Page
I. Introduction	249
II. Description of comparator	250
III. Gage holders	250
IV. The micrometer caliper	251
V. Results of a set of measurements	253
VI. Sources of error	254
1. Lack of alignment of the measuring faces	254
2. Defective alignment of gages	254
3. Influence of foreign bodies between the measuring surfaces of the ends of the gage	254
4. Friction in tailstock	255
VII. Conclusion	255

I. INTRODUCTION

Apparatus for comparing a length gage having spherical ends with one having plane ends where the difference in the thermal expansion is large has been developed and several comparisons have been completed. The need for making the intercomparison of gages arose in connection with the measurement of the diameters of some single-layer solenoids which were used as absolute standards of self-inductance. The diameters of the solenoids have been measured at 30° C. by comparison with a gage or end standard using an electrically controlled micrometer caliper [1] which operates with a measuring pressure of about 150 g. In making the comparison between the solenoid and a gage it is essential to use a gage with spherical ends, since it is not feasible to align a gage with plane ends between the faces of the micrometer with sufficient accuracy. At this bureau, the lengths of

[1] Moon, Charles, J. Opt. Soc. Am. and Rev. Sci. Inst., vol. 11, p. 453, 1925.

gages with plane ends are determined at 20° C. by interferometer methods.[2] The present work was undertaken to determine the length at 30° C. of the gage with spherical ends in comparison with a plane-ended gage which had been measured at 20° C. in terms of the wave lengths of light.

The only gages with plain ends now available are made from steel having a coefficient of expansion ranging from 11 to 14 parts in 1,000,000 per °C. Long gages hardened on the ends only have a coefficient near tbe lower limit of the above range. For this work, gages with spherical ends were made both from steel and from fused quartz, the latter having a temperature coefficient of only 5 parts in 10,000,000 per °C. An intercomparison was first made at 20° C. between a calibrated steel gage with plane ends and a fused quartz gage with spherical ends. This gave the length of the quartz gage at 20° C. The length of the quartz gage at 30° C. was computed from the known temperature coefficient. The two gages were also compared at 30° C. so that the coefficient of expansion of the steel gages could be computed.

An electrically controlled micrometer caliper is especially suitable for the comparison of gages having a large difference of linear expansion, since it can be used to make measurements within a small closed space where the temperature can be accurately controlled. In this work there is the added advantage of having the end standards calibrated under the same conditions as that in which they were later used in measuring the diameter of the solenoids where the working pressure must necessarily be very light to prevent deformation of the copper winding. A suitable comparator for the calibration of gages has been made by mounting the micrometer ring and a gage holding device on a common base.

II. DESCRIPTION OF COMPARATOR

The general arrangement of the comparator is shown in Figure 1. A cast-iron bed supports the micrometer caliper and two gage holders. The ring of the micrometer caliper is mounted on three slender leveling screws which are rigidly fastened to the bed. The tops of these screws rest in a 3-point support of the point-slot-plane type. This support holds the micrometer in a fixed position with regard to the bed, but is sufficiently flexible so that any expansion of the bed will not deform the ring. The gage holders are mounted on a cross slide, the base of which is rigidly clamped to the bed. Since the bed serves only as a firm support for the gage holder and micrometer ring, it does not need to have precision ways. When in use the whole comparator is inclosed in a small insulated cabinet with thermostatic control of temperature.

III. GAGE HOLDERS

The gage holders are mounted on a carefully made cross slide. Each holder is capable of supporting either a rectangular gage or a cylindrical gage, as shown in Figure 2. In either case, the gages rest on steel balls which roll on grooved steel blocks and allow an easy endwise motion in a fixed line. The steel blocks are mounted on a

[2] Peters, C. C., and Boyd H. S., Interference Methods for Standardizing and Testing Gage Blocks, B. S. Sci. Papers, vol. 17, p. 677, 1922.

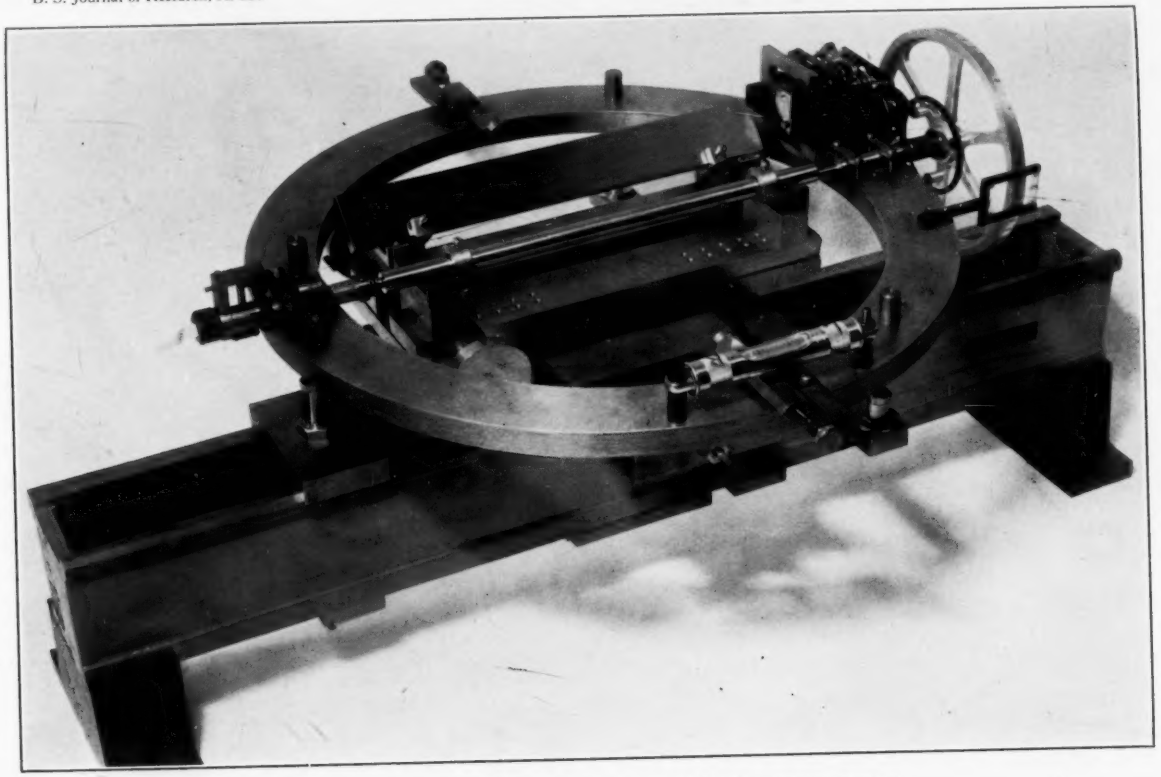


FIGURE 1.—*Comparator with gages in position for measurement*

flat bar which is attached to the top of the cross slide. One end of the bar is hinged to the cross slide by a thin steel spring while the other end can be moved horizontally or vertically by tangent screws with graduated heads. The ways of the cross slide are accurately straight so that once a gage is correctly aligned it can be moved from the measuring position and returned to it without change in alignment. The screw which moves the cross slide and also the tangent screws can be turned by keys which extend through the walls of the constant temperature cabinet.

IV. THE MICROMETER CALIPER

The electrically controlled micrometer caliper has many of the features of the one previously described.[3] The mechanical design

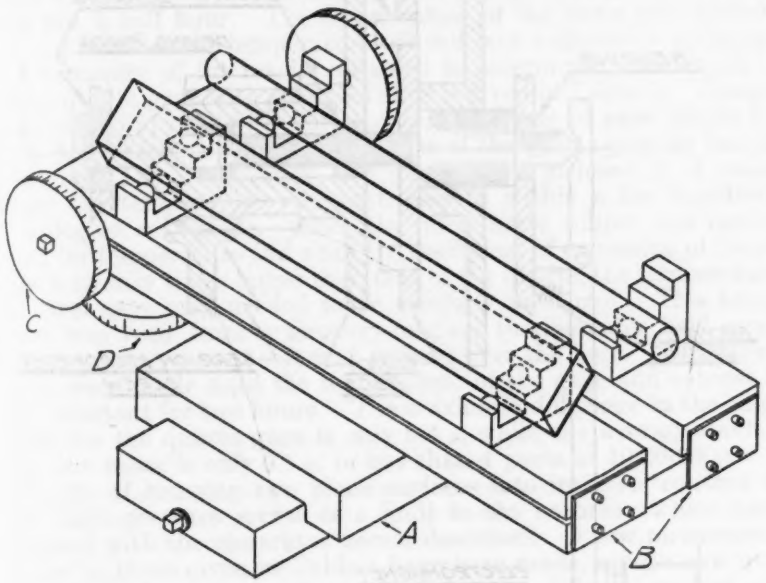


FIGURE 2.—*Gage holders*

A, cross slide; *B*, steel spring hinges; *C* and *D*, tangent screws.

has been changed by a new device for automatically stopping the screw, and temperature compensation has been accomplished by the use of a nickel-steel ring. In order that these modifications may be easily understood, a brief description of the instrument will be given.

A precision micrometer head and a spring-controlled anvil which operates an electrical contact are mounted on a diameter of a ring of nickel steel. The micrometer is driven slowly through a train of gears by a motor which operates on about two watts at three volts. When a gage is so mounted between the screw and anvil that only a small force is required to move it in the direction of its axis, the advancing screw of the micrometer pushes the gage against the anvil until the force is sufficient to open the platinum-iridium contacts operated by the anvil. The opening of this contact releases a mag-

[3] Moon, Charles, J. Opt. Soc. Am. and Rev. Sci. Inst., vol. 11, p. 463, 1925.

netic clutch in the train of gears which drives the micrometer screw, thus stopping the motion of the screw. The position at which the micrometer stops is read directly from the micrometer scale. The micrometer can be turned back to make a new reading by means of a switch, which reverses the motor and reengages the clutch.

One of the new features of this micrometer is the magnetically operated clutch which is shown in Figure 3. Its action is due to the friction between a smooth steel disk and three pieces of cork inserted in another similar disk. When a current is flowing in the electromagnet, the two disks are pressed together and rotate at a speed of

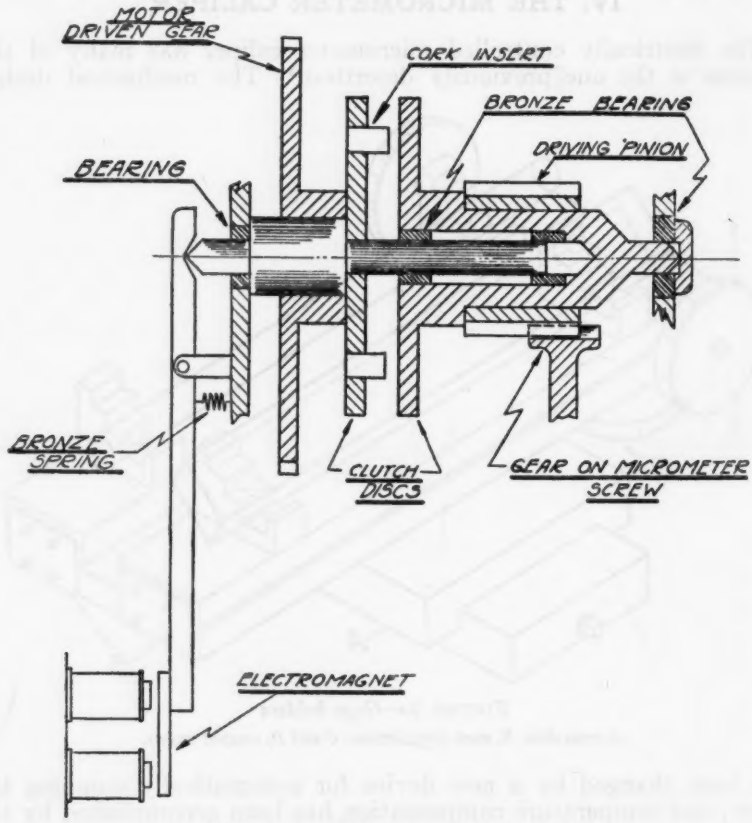


FIGURE 3.—*Electromagnetic clutch*

six revolutions per minute or less. At this low speed the micrometer screw, which rotates at one-tenth the speed of the pinion, stops so quickly when the current is interrupted that the speed of the motor is of little importance. A change of the speed from 500 to 2,500 revolutions per minute does not affect the setting of the micrometer by as much as 0.1μ.

The nickel-steel ring has a coefficient of expansion of about 3 parts in 1,000,000 per °C., whereas the steel of which the micrometer and anvil are constructed has a coefficient of expansion of about 12 parts in 1,000,000. The design is such that the length of nickel steel which affects the readings is about four times that of the steel. Hence with

a change of temperature there is very little change in the distance between the faces of the micrometer.

The micrometer has a large head graduated to read microns, divisions being about 1 mm apart; 0.1μ can be estimated and settings are automatically repeated to this order of magnitude. The anvil is pushed forward by a spring, thus pressing the contact operated by the anvil against the fixed contact. When the force on the face of the anvil exceeds the force exerted by the spring the contacts open. In the micrometer shown in Figure 1 the force required to open the contacts is 150 g.

V. RESULTS OF A SET OF MEASUREMENTS

In making a comparison of the length of two gages, three sets of three readings each were made on both gages. The interval between sets was a half hour. The mean values of the three sets agreed to 0.1 μ, provided the temperature control was sufficiently accurate.

A summary of the results obtained in determining the length of a 28 cm quartz gage with spherical ends is given in Table 1. This gage has been compared with different combinations of gage blocks built up to have a length differing from that of the quartz gage by less than 0.3 mm. The comparator and gages were inclosed in a cabinet where the temperature was controlled to within a few hundredths of a degree centigrade. Since the micrometer caliper was compensated for temperature and since the coefficient of expansion of the steel gage is twenty times larger than that of the quartz, the temperature of the steel gage only needed to be carefully measured. This temperature was read from a mercury-in-glass thermometer held against the gage by a mass of soft wax pressed over the bulb. No measurements were made until the temperature of the gage and cabinet had been constant for two hours. The maximum difference in the lengths found for the quartz gage is only 0.4 μ, while the average deviation from the mean is only 0.1 μ, or less than 4 parts in 10,000,000. The difficulty of bringing two plane surfaces into intimate contact with very light pressure serves as a limit to the accuracy which can be obtained with the apparatus herein described. A few measurements similar to those given in Table 1 have been made, using a new quartz gage made from material obtained from a different source. The mean result of several measurements would indicate that the new quartz rod has a coefficient of expansion about 0.03×10^{-6} less than the rod used to obtain the results given in Table 1.

TABLE 1

Date of measurement	Temperature of cabinet	Nominal lengths of steel gages at 20° C.	Certified length of steel gages corrected to cabinet temperature	Measured length of quartz gage
1931	°C.	mm	mm	mm
May 27	20.02	275.0+1.9+1.7+1.6	280.2004	280.2654
May 28	19.90	275.0+3.0+1.9	279.9000	280.2658
June 6	19.75	275.0+1.9+1.8+1.6	280.2996	280.2657
June 8	20.10	275.0+1.9+1.8+1.6	280.3006	280.2656
August 8	20.24	275.0+1.6+1.7+1.9	280.2010	280.2655
August 9	20.00	275.0+1.6+1.7+1.9	280.2003	280.2656
August 16	19.98	275.0+2.5+1.9+1.6	[1] 281.0002	280.2653

[1] 2.5 mm gage block has never been standardized at the Bureau of Standards.

As comparisons of the steel and quartz gages were made at both 20° and 30° C., the temperature coefficient of expansion of the steel gage was computed on the assumption that the coefficient of expansion of fused quartz [4] is 0.4×10^{-6} per °C. The value of the coefficient, 11.0×10^{-6} per °C. for the steel gages, lies in the range of values found by other observers [5] for gage steels.

VI. SOURCES OF ERROR

Since many of the sources of error in length measurement are common to all measuring machines, the discussion here is limited to a few important causes and the corrective methods which were adopted.[6]

1. LACK OF ALIGNMENT OF THE MEASURING FACES

The measuring faces of the screw and anvil of the micrometer are not strictly planes, but convex spherical surfaces having a radius of 10 m. At 1 mm off the axis, this surface would curve away from a plane by approximately 0.05 μ. The faces are carefully made so that the center of the spherical surface of the anvil lies in the axis of the plunger, and the center of the spherical surface of the micrometer screw lies in the axis of the screw. The grooves in the micrometer ring, in which the screw and anvil are clamped, were first carefully lapped to bring the two axes nearly parallel. The lack of adjustment was determined by measurements on a spherical-ended gage placed at different points between the measuring surfaces. Adjustments in alignment were accomplished by changing the pressure on the clamps which hold the anvil and screw in position. By repeated trials an adjustment was reached so that a movement of the axis of the spherical-ended gage of about 1 mm in any direction perpendicular to its axis did not change the readings of the micrometer by more than 0.1 μ.

2. DEFECTIVE ALIGNMENT OF GAGES

The error due to defective alignment of gages depends on the type of gage which is being used. The spherical-ended gages could be aligned by sight with sufficient accuracy. The flat-ended gages were aligned by taking a series of micrometer readings for different settings of the horizontal and vertical tangent screws, then setting the tangent screws to a position which gave a minimum reading of the micrometer. By making the alignment in this manner, a measurement on realignment agreed with the original within 0.1 μ.

3. INFLUENCE OF FOREIGN BODIES BETWEEN THE MEASURING SURFACES AND THE ENDS OF THE GAGE

Before placing the gage in the comparator, both the ends of the gage and the measuring surfaces of the micrometer were carefully cleaned to remove any foreign bodies, such as dust, from the surfaces. With spherical-ended gages consistent readings were readily obtained after they were cleaned with ordinary care. With flat-ended gages, however, consistent readings at the pressure of 150 g could not be

[4] Souder and Hidnert, Measurements of Thermal Expansion of Fused Silica, B. S. Sci. Paper, vol. 21, p. 1, 1926.
[5] Souder and Hidnert, Thermal Expansion of a Few Steels, B. S. Sci. Papers, vol. 17, p. 611, 1922.
[6] A discussion of errors in length measurements is given by F. H. Rolt in Gages and Fine Measurements (MacMillan & Co. 1929), vol. 1, chs. 6, 16, and 17.

obtained even after the most careful cleaning when the measuring surfaces were brought directly against the surfaces of the gage. To obtain reproducible results with flat-ended gages, the measuring faces were set against the gage with the normal measuring pressure, then the cross slide was moved slightly back and forth two or three times. This action tended to remove or distribute foreign material, after which consistent readings could be obtained.

4. FRICTION IN TAILSTOCK

It is necessary that the plunger to which the anvil is attached work very freely in the tailstock since any friction causes a variation in the measuring pressure. While the total measuring pressure is only 150 g, this force is sufficient to distort the ring 1 μ; so that a variation of 15 g would cause a difference in reading of 0.1 μ. These readings on the gages repeated so well that there was no reason to suspect a variation in measuring pressure.

VII. CONCLUSION

With the apparatus described, the length of a spherical-ended gage of quartz can be compared with a flat-ended gage of steel with an accuracy of about 1 part in 1,000,000 on 30 cm gages, using a very light measuring pressure of only 150 g. Since a large part of the error occurs in the readings on the steel gages, somewhat higher accuracy can be obtained in the comparison of two spherical-ended gages of the same material, or in the comparison of two similar flat-ended gages which would permit the use of spherical measuring faces.

WASHINGTON, December 23, 1932.

CLAY IN CONCRETE

By D. A. Parsons

ABSTRACT

The effect on the compressive strength, absorption, and permeability of concretes of substituting clay either for 10 per cent of the volume of the cement or for 7½ per cent of the volume of the fine aggregate were studied. A basic mix without clay and containing five bags of cement per cubic yard of concrete served as a reference. All concretes were of the same consistency as determined by a penetration test. Three different cements and three different clays were used in a number of combinations. All specimens were kept in damp storage at 70° F. for 28 days and thereafter some were stored outdoors and the rest were subjected to freezing and thawing. Specimens were tested for compressive strength at the ages of 7 and 28 days and for strength, absorption, and permeability at 3, 6, and 9 months, and 1, 2, and 3 years.

The substitution of clay for 10 per cent of the volume of the cement caused a small (zero to 10 per cent) decrease in the compressive strength of the concrete at ages greater than three months. The permeability was not changed appreciably.

Substituting clay for 7½ per cent of the volume of the fine aggregate increased the compressive strength of the concrete from 1 to 37 per cent. The permeability at the early test ages was decreased but increased at later ages both actually and relative to the concrete without clay. All of the concretes were practically impermeable in these tests.

The replacement of 7½ per cent of the sand in one case and 10 per cent of the cement in the other by equal volumes of clay slightly increased the absorption for those specimens stored outdoors, but did not appreciably change that of specimens frozen and thawed.

The clay admixtures had no apparent effect on the resistances of the concretes to freezing and thawing exposure as no disintegration took place among those which were kept damp. All of the specimens, with and without clay, which were subjected both to an occasional drying and to freezing and thawing exposure were disintegrated.

The differences in absorption, permeability, and resistance to freezing and thawing between concretes containing and not containing clay were small.

CONTENTS

	Page
I. Introduction	258
1. Purpose	258
2. Outline of investigation	258
II. Materials	259
1. Cements	259
2. Sand	259
3. Coarse aggregate	260
4. Clays	260
III. Preparing the concrete	260
1. Treatment of materials	260
2. Proportioning and mixing	261
IV. Properties of the fresh concrete	261
1. Workability	261
2. Weight per unit volume	261
V. Test specimens and storage	263
1. Specimens	263
2. Conditions of storage	263
VI. Results of tests	264
1. Compressive strength	264
2. Absorption	267
3. Resistance to freezing and thawing	268
4. Permeability	269
VII. Conclusions	273
VIII. Acknowledgements	273

I. INTRODUCTION

1. PURPOSE

The investigation described herein was conducted at the Bureau of Standards, Washington, D. C., with the cooperation of Hugh L. Cooper & Co. (Inc.), New York, N. Y.

An effort was made in this study to determine the value of clay as an admixture in concrete of a type commonly used in construction and was one of several investigations of the same nature sponsored by Col. Hugh L. Cooper.

The qualities of concrete which were measured were compressive strength, absorption, resistance to a freezing and thawing exposure, and permeability to water under pressure.

2. OUTLINE OF INVESTIGATION

Three general types of concrete were made which are designated by the Roman numerals: I, II, and III. No. I contained no added clay. No. II had the same proportions of dry ingredients as No. I except that clay was substituted for 10 per cent (by volume) of the cement. No. III had the same dry ingredients as No. I except that 7½ per cent of the dry rodded volume of the sand was replaced by an equal volume of clay.

It was specified that: (1) The dry rodded volume of the sand should be 1.15 times the volume of the voids in the coarse aggregate for the plain concrete and for that in which 10 per cent of the cement was replaced by clay, (2) the plain concrete and that in which 7½ per cent of the sand was replaced by clay should have a cement content of five bags per cubic yard, and (3) the consistency of all mixes should be such that a man walking in a large mass of the fresh concrete would sink to a depth greater than 3 inches and less than 8 inches.

Condition No. 3 relative to consistency would have required the production of concrete on a field scale in order to make a satisfactory test. As this was not feasible the water content of mix No. I, plain concrete without clay, was varied, using one-tenth cubic yard batches, until a consistency was obtained which was judged to satisfy the requirement. The amounts of water to use with mixes II and III, containing clay, were then determined by trial such that their workabilities as measured by the penetration test described in Section IV were the same as for mix No. I. The proportions are given in Table 1.

TABLE 1.—*Proportions of concrete*

Method	Mix	Cement	Water	Clay	Sand	Crushed rock
Parts by bulk volume	I	1	1.07	0	2.02	4.40
	II	1	1.22	.11	2.25	4.89
	III	1	1.11	.15	1.87	4.40
Parts by weight	I	1	.71	0	2.22	4.77
	II	1	.81	.08	2.46	5.30
	III	1	.74	.11	2.05	4.77
Percentage by weight	I	11.49	8.15	0	25.50	54.86
	II	10.35	8.37	.88	25.51	54.90
	III	11.53	8.49	1.30	23.65	55.03
Percentage by absolute volume	I	8.8	19.7	0	23.2	48.3
	II	7.9	20.1	.8	23.1	48.1
	III	8.8	20.4	1.2	21.4	48.2

Three complete sets of specimens were made using three different brands of cement. In addition, three complete sets of those containing clay were made using three different kinds of clay. In all, there were 21 distinct mixtures.

Specimens of each mixture were made for testing in compression at the ages of 7 and 28 days (after storage in a damp closet) and 3, 6, and 9 months and 1, 2, and 3 years after storage out of doors. Absorption and permeability test specimens were prepared for testing first at age 3 months and then retesting at the ages of 6 and 9 months and 1, 2, and 3 years.

In order to provide for two types of exposure, namely, out of doors and freezing and thawing, additional specimens were made for those tests later than age 28 days, all specimens being kept for the first 28 days in damp storage.

For each different mixture and storage condition (and age in the case of the compressive test specimens) 3 compressive, 3 absorption, and 6 permeability test specimens were made, or a grand total of 1,260 specimens.

II. MATERIALS

1. CEMENTS

Cement No. 1 was a finely ground, high early-strength Portland. Nos. 2 and 3 were ordinary Portlands, No. 2 being a smooth, easy working cement, and No. 3 a harsh cement as indicated by previous tests [1] made at the Bureau of Standards. All complied with the requirements of the Federal Specification SS–C–191 for Cement, Portland. The specific gravities [2] were 3.137, 3.135, and 3.178, respectively, and the percentages of water required for normal consistency were 25.8, 23.0, and 22.2, respectively.

2. SAND

Potomac River sand, all obtained at the same time, was used throughout. A summary of the properties of the sand is given in Table 2.

TABLE 2.—*Properties of the sand* [a]

Passing sieve No.	Percentage, by weight
4	99
8	92
16	78
30	57
50	15
100	3

Fineness modulus	2.56
Percentage, by weight, removed by decantation	2.4
Percentage of water absorption by weight in 30 minutes	.7
Percentage of voids (dry rodded condition)	37.8
Pounds per cubic foot (dry rodded condition)	103
Apparent specific gravity	2.656

[a] The test methods used were those of the American Society for Testing Materials, as follows:
C 41-24, 1930 Book of A. S. T. M. Standards, II, p. 155.
D 136-28, 1930 Book of A. S. T. M. Standards, II, p. 618.
C 30-22, 1930 Book of A. S. T. M. Standards, II, p. 153.
C 29-27, 1930 Book of A. S. T. M. Standards, II, p. 151.
D 55-25, 1930 Book of A. S. T. M. Standards, II, p. 614.
The apparent specific gravity of the sand was determined by the use of Le Chatelier flasks and water, the final readings being taken 18 minutes after immersing the material. The values were adjusted for temperature, those given corresponding to a temperature of 4° C.

[1] P. H. Bates and J. R. Dwyer, Cement as a Factor in the Workability of Concrete, Proc. Am. Conc. Inst., vol. 24, p. 43, 1928.

[2] Determined on samples previously dried at 115° C. using Le Chatelier flasks and alcohol. All values were adjusted for temperature, those given corresponding to a temperature of 4° C.

3. COARSE AGGREGATE

The crushed rock was very dense limestone quarried at Martinsburg, W. Va. The sieve analysis (with square opening sienes) showed 98.5 per cent by weight finer than 1½ inches, 63.2 per cent finer than ¾-inch, 33.1 per cent finer than ⅜-inch, and 1.1 per cent finer than a No. 4 sieve. Additional data on the physical properties of the coarse aggregate are given in Table 3.

TABLE 3.—*Physical properties of coarse aggregate* [a]

Fineness modulus	7.05
Percentage of water absorption by weight in 24 hours	.2
Percentage of voids (dry rodded condition)	40.3
Pounds per cubic foot (dry rodded condition)	102
Apparent specific gravity	2.737

4. CLAYS

The selection of the clays used in the investigation was made with the object of obtaining materials which when mixed with water would give "short," "medium plastic," and "plastic" mixtures. In this order they were: No. 1. A red surface clay from Occoquan, Va.; No. 2, a blue clay from Baltimore, Md.; and No. 3, a yellow clay from Alexandria, Va. The percentage by weight passing a No. 200 sieve (washed), the percentage by weight loss on ignition (after drying at 110° C.), and the specific gravity [3] for No. 1 clay were 76, 7.1, and 2.690; for No. 2 clay 93, 5.0, and 2.658; and for No. 3 clay 95, 5.0, and 2.698, respectively.

As these clays were all used in the manufacture of brick they probably were relatively free from the organic materials that are usually found near the surface of the ground, but it appears that a test in mortar or concrete is the only sure and practical method known of determining the suitability of a clay in this respect. The 7 and 28 day compressive strength results obtained with concretes containing the three clays indicated that they contained little if any injurious organic material.

The weights of all clays when dry and pulverized were found to be about 70 pounds per cubic foot and this value was used in proportioning the concretes.

III. PREPARING THE CONCRETE

1. TREATMENT OF MATERIALS

The cements were stored in air-tight steel barrels (of six or seven bag capacity) until used.

The sand and rock after drying were stored in bins indoors, the crushed rock being separated into three sizes by means of a rotary screen.

The clays were dried in lumps on the laboratory floor, pulverized in a dry pan to pass a No. 14 sieve and stored in a dry place in canvas bags. All proportioning was done by weight.

---

[a] The test methods used were those of the American Society for Testing Materials as follows:
C 41–24, 1930 Book of A. S. T. M. Standards II, p. 155.
C 29–27, 1930 Book of A. S. T. M. Standards II, p. 151.
D 30–18, 1930 Book of A. S. T. M. Standards II, p. 612.
The apparent specific gravity was determined also by using Le Chatelier flasks and water, making the final readings 18 minutes after immersion.

[3] Using the same methods as for the cements. See footnote 2, p. 259.

2. PROPORTIONING AND MIXING

The proportions of the materials used in the several mixes are shown in Table 1. Altogether there were 21 concretes differing from each other either in clay content, kind of clay, or brand of cement. In order to minimize the effects of uncontrolled factors having seasonal variations the general plan of mixing adopted consisted in the division of the work into three parts such that when one-third or two-thirds of the total number of specimens had been made all of the 21 concretes were equally represented. The mixing was done in a one-tenth cubic yard capacity Wonder mixer having a speed of 13 r. p. m. The capacity was such that two batches were required to make one-third of the specimens for one concrete. Fabrication was started in April and finished in November. After weighing all materials the crushed rock, sand, and cement were placed in the mixer in the order named. Immediately thereafter the clay and water, thoroughly mixed together, were added. The period of mixing was two minutes after all materials were in the mixer.

IV. PROPERTIES OF THE FRESH CONCRETE

1. WORKABILITY

The time required for making the workability measurements was about 15 minutes per batch. The slump test was made according to standard methods [4] except that the slump cone had a top diameter of 3½ inches instead of 4. The penetration test as given below was considered to give a true index of the workability and for this test the whole batch was used.

The fresh concrete was placed in a 20-inch diameter container to a depth of 14½ inches. A rectangular area 12 by 3 inches bearing on the surface of the concrete was loaded with a 160-pound weight. The average penetration of three trials was taken as a measure of the workability of the batch.

TABLE 4.—*Average values from workability tests*

Mix	Slump	Flow	Penetration
	Inches	*Per cent*	*Inches*
I. Plain concrete (without clay)	4.0	49	2.3
II. 10 per cent of the cement replaced by clay	3.0	47	2.3
III. 7½ per cent of the sand replaced by clay	2.1	41	2.3

While making the slump and flow tests it was noticed that the change in the shape of the mass was frequently more like a sliding or crumbling action than a true slump or flow. This was particularly true for the concretes not containing clay.

2. WEIGHT PER UNIT VOLUME

After the workability tests were made a dekaliter container was filled and weighed. The concrete was placed in three layers, each layer being rodded until fine material appeared around the edge.

[4] The slump test is described in Proc. Am. Soc. Test. Mat., vol. 26, pt. 1, p. 874, 1926. The flow tests were made by the methods described in the Standard Methods of Making Compression Tests of Concrete (C 39-27), 1930 Book of A. S. T. M. Standards, II, p. 143 except that the drop of the table was one-eighth inch instead of one-half inch.

The weight of the concrete divided by the volume of the container gave the weight per unit volume. The number of bags of cement per cubic yard of concrete was then computed by the use of the following formula:

Bags of cement per cubic yard=(percentage cement, by weight in the mix × (weight per cubic foot of fresh concrete) × 27/94

With the assumption that there were no air voids, the weight per cubic foot was calculated from the weight percentages and the apparent specific gravities of the materials. Thus, the calculated weight per cubic foot of fresh concrete equals:

$$\frac{62.428 \times 100}{\sum \frac{\text{Percentage by weight of material}}{\text{Apparent specific gravity}}}$$

NOTE.—No allowance was made for the absorption of water by the aggregate because the values for apparent specific gravities here used and given elsewhere are weights per unit volume of materials exclusive of the voids or pores accessible to water.

The air voids were determined by means of the equation:
Percentage of air voids equals:

$$\frac{\text{Computed weight per cubic foot} - \text{actual weight per cubic foot}}{\text{Computed weight per cubic foot}}$$

While it is theoretically possible to calculate the amounts of air and water voids in concretes by means of these formulas, the results are apt to be in error because of differences between the proportions in the mixer and in the concretes of the specimens. There was loss of water by evaporation and also a loss of water, cement, and the finer portions of the aggregate by adherence to the mixer, dumping pan, and tools. The values shown in Table 5 are averages of the individual observations for the batches immediately preceded by identical batches, in which case the mixer and the pan were not washed out.

It is reasonable to believe that the values for air voids should be slightly higher and those for cement factor slightly lower.

TABLE 5.—*Properties of the fresh concrete*

Mix	Weight of fresh concrete		Air voids	Air and water voids	$\frac{C}{V+C}$ [1]	Bags of cement per cubic yard
	Measured	Computed				
	*Lbs./ft.*³	*Lbs./ft.*³	*Per cent*	*Per cent*		
I. Plain concrete (without clay)	150.18	150.59	0.3	19.3	0.314	4.958
II. 10 per cent (by volume) of cement replaced by clay	149.27	149.84	.4	19.8	.285	4.438
III. 7½ per cent (by volume) of sand replaced by clay	149.78	149.84	.0	19.8	.307	4.960

[1] Cement-voids ratio where C= absolute volume of cement, and V= volume of air and water voids.

V. TEST SPECIMENS AND STORAGE

1. SPECIMENS

Six by twelve inch cylinders were used for all compressive strength and absorption tests. They were cast in doubly paraffined paper molds. The concrete was placed in three layers and each layer rodded with a ⅝-inch diameter steel rod, having a bullet-shaped end, until the fine material appeared around the edge of the mold.

The permeability specimen was a cylinder of diameter 8 inches and height 9 inches. At the center, surrounded in all directions by about 3¼ inches of concrete, was a 1½-inch diameter paper carton (length, 2½ inches) filled with damp sand. A ¼-inch galvanized-iron pipe threaded on the top end extended into the center of the damp sand and protruded about 1½ inches above the cylinder. It was the means of conveying the water under pressure to the center in making the permeability test. These specimens were cast in steel molds. The procedure consisted in placing two tamped layers of concrete having a combined depth of about 5 inches, inserting the paper carton filled with damp sand, and then adding more concrete to make the total depth 9 inches. A shell of rich mortar was placed directly in contact with the ¼-inch pipe leading to the top of the specimen from the paper carton.

At the time of mixing it was thought that the shell of rich mortar immediately adjacent to the pipe would aid in preventing leakage along the outside of the pipe, but during the tests many of the specimens leaked at this place. This water was not considered as having passed through the concrete and was therefore not included in the measured leakage.

2. CONDITIONS OF STORAGE

Neither the temperature of the materials in the mix nor the temperature of the mixing room was closely controlled; however, all specimens except those for permeability tests were taken to a constant temperature (70° ± 2° F.) room within three hours after molding and remained there for 20 to 24 hours. They were then removed from the molds, the permeability specimens wire brushed on their vertical sides, and all taken to a 90 per cent or greater relative humidity, constant temperature (70° ± 2° F.) room for curing.

Specimens used for 7 and 28 day compressive strength tests were tested as soon as taken from the damp closet. The specimens stored outdoors after the 28-day damp curing period were brought into the laboratory for one week before testing in order to minimize the variations in moisture content. The specimens that had been frozen and thawed were tested within an hour after removal from water. The set of specimens subjected to freezing and thawing were frozen in air and thawed in water. The usual cycle was 20 to 22 hours in the freezing chamber and 2 to 4 hours in water. The specimens were not at any time permitted to dry, with the exception of those cylinders used for absorption determinations. The minimum air temperatures in the freezing room for any cycle varied from −5° to +23° F., but were usually between +10° and +20° F. Figure 1 shows the results of measurements made on two different days of the air and concrete

temperatures in the freezing chamber. The temperature of the concrete was determined by thermocouples embedded in the center of the 6 by 12 inch cylinders.

VI. RESULTS OF TESTS

1. COMPRESSIVE STRENGTH

The cylinders used for compressive tests at ages up to and including one year with few exceptions were prepared for test by grinding the ends to plane surfaces. Those tested at the age of 2 years were

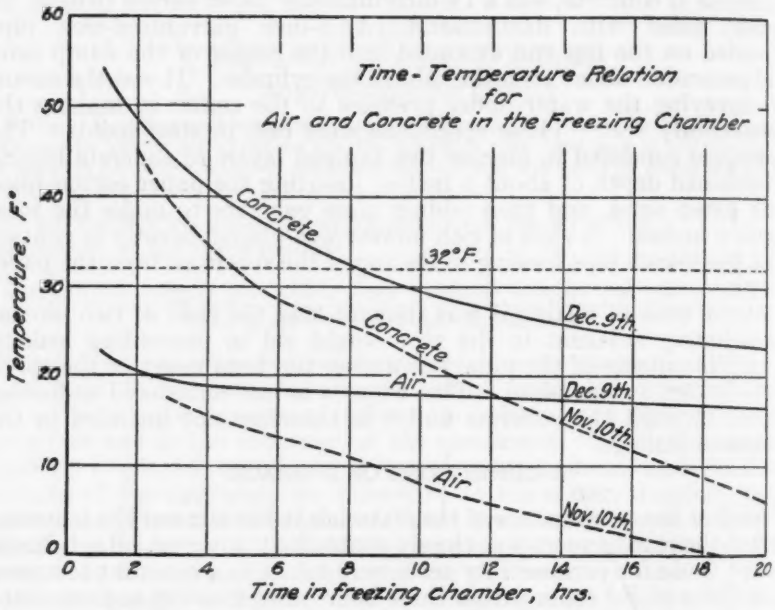


FIGURE 1.—*Temperatures in the freezing and thawing tests*

capped the day before the test with a rich high early strength Portland cement mortar. The capped outdoor specimens probably gave values a little lower than would have been obtained by the original method.

The data are given in Figures 2, 3, and 4 where the plain concrete without clay represents the average of three tests. Since there were no significant differences found between the compressive strengths of the concretes containing different clays the results obtained for all were averaged for the purpose of comparison with the plain concrete. Hence for each plotted point representing concrete containing clay, three times the number of specimens were used for its determination as were used for the corresponding point for the plain concrete.

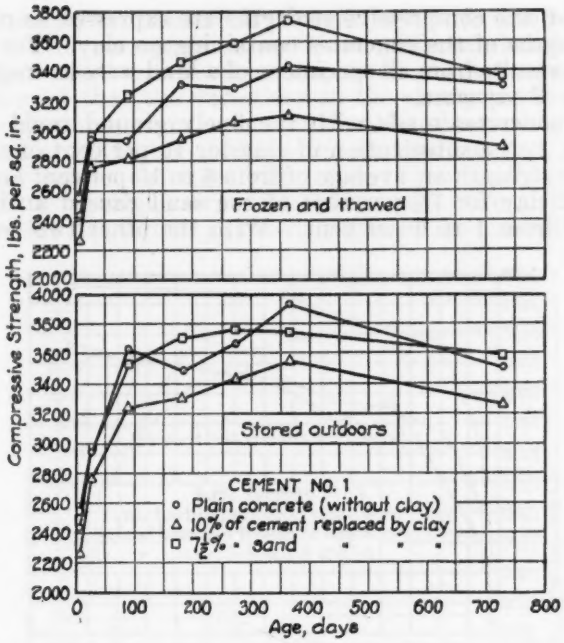

Compressive Strength, lbs. per sq. in.
Frozen and thawed
Stored outdoors
CEMENT NO. 1
Plain concrete (without clay)
10% of cement replaced by clay
7½% " sand " " "
Age, days

FIGURE 2.—*Age-compressive strength relations of concretes I, II, and III with cement No. 1*

TABLE 6.—*Effect of clay admixtures on compressive strength*

Concrete	Cement content	Water/cement [1] by volume	Compressive strengths in per cent of concrete No. I without clay at ages of—						
			7 days	28 days	3 months	6 months	9 months	1 year	2 years
	Bags/yd.[3]		*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
CEMENT NO. 1									
I. No clay	4.96	1.03	100	100	100	100	100	100	100
II. 10 per cent of cement replaced by clay	4.44	1.18	93	94	92	92	93	90	90
III. 7½ per cent of sand replaced by clay	4.96	1.07	105	101	103	105	106	102	102
CEMENT NO. 2									
I. No clay	4.96	1.03	100	100	100	100	100	100	100
II. 10 per cent of cement replaced by clay	4.44	1.18	109	113	104	94	96	97	100
III. 7½ per cent of sand replaced by clay	4.96	1.07	131	137	125	114	118	116	114
CEMENT NO. 3									
I. No clay	4.96	1.03	100	100	100	100	100	100	100
II. 10 per cent of cement replaced by clay	4.44	1.18	100	101	104	96	97	98	99
III. 7½ per cent of sand replaced by clay	4.96	1.07	119	113	117	106	112	112	109

[1] Corrected for absorption of the aggregate.

In Table 6 the compressive strengths are expressed as percentages of the strengths of the concretes containing no clay. For this comparison the results from all specimens of a kind were averaged regardless of type of exposure.

For the concretes made with the finely ground rapid hardening cement No. 1, the substitution of clay for 10 per cent of the cement reduced the strength an average of from 8 to 10 per cent and the substitution of clay for 7½ per cent of the sand caused an increase in strength of from 1 to 6 per cent. With the other two cements the

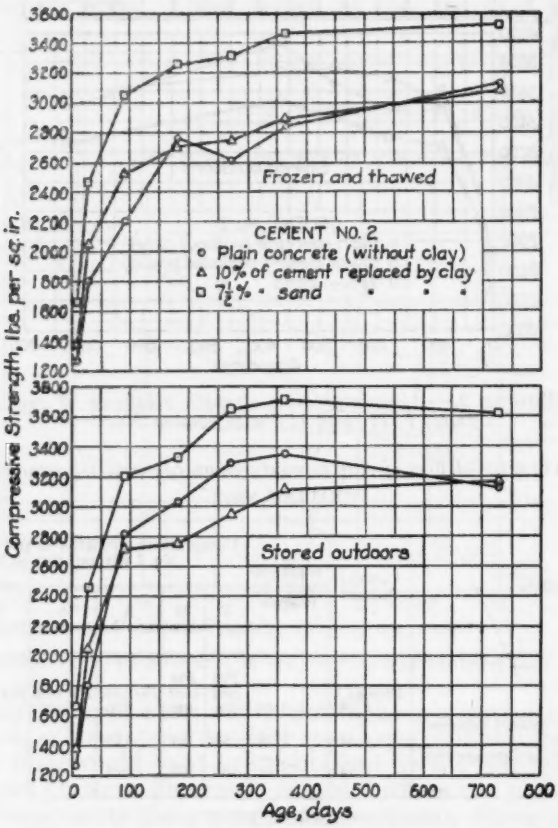


FIGURE 3.—*Age-compressive strength relations of concretes I, II, and III with cement No. 2*

substitution of clay for 10 per cent of the cement had practically no effect, but the substitution for 7½ per cent of the sand caused an appreciable increase in strength varying from 6 to 37 per cent. With all cements, the ratio of the strengths of concretes II and III containing clay to the strength of concrete I without clay tended to become smaller with an increase in age.

Statistical measures of the dispersions of the compressive strength data for the three types of concrete (I, II, and III) were calculated to determine the effect of the clays on the uniformity of the concretes. Two measures of the dispersions for each type of concrete were com-

puted. One was a measure of the dispersion in the strengths of specimens of like composition but from different batches and the other of the variations among specimens of the same batch. Both of these showed that the variations in the strengths of cylinders of concretes containing clays were less than for those of concrete containing no clay. On the average the dispersions were about one-fourth larger for the concretes without clay than for those containing a clay admixture. However, as the differences between the statistical measures of the dispersions in the strengths of the concretes with and

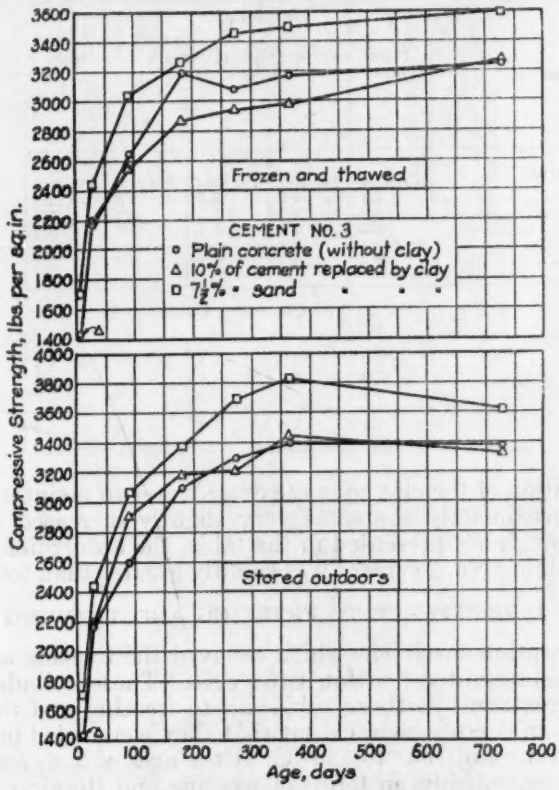

Compressive Strength, lbs. per sq. in.
Frozen and thawed
CEMENT NO. 3
○ Plain concrete (without clay)
△ 10% of cement replaced by clay
□ 7½% " sand " " "
Stored outdoors
Age, days

FIGURE 4.—*Age-compressive strength relations of concretes I, II, and III with cement No. 3*

without clays were only from 1.0 to 2.6 times the probable errors of the differences, the data do not show positively that the additions of clays improved the uniformity of the concretes. That is, the differences in the uniformity were only large enough in comparison to the precision of the statistical measures to give a strong indication that the apparently beneficial results of the clay admixtures were not due to chance.

2. ABSORPTION

In making water-absorption determinations at the ages indicated in Table 7, 6 by 12 inch cylinders were dried in a gas oven at temperatures varying between 100° and 130° C. for three days and subse-

quently immersed in water for three days. The absorption was computed as the difference between the dry weight and the weight after immersion, expressed as a percentage of the dry weight. Each value in Table 7 is an average of the results obtained from 9 specimens, 3 each from 3 cements. The cylinders used for the three months' test were retested at the ages of 6 and 9 months to give the values shown.

TABLE 7.—*Absorption of the concretes*

FROZEN AND THAWED

Age	I	II			III		
	Plain concrete	10 per cent of cement replaced by clays Nos.—			7½ per cent of sand replaced by clays Nos.—		
		1	2	3	1	2	3
MONTHS	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
3	5.1	4.9	5.0	5.3	5.1	5.3	5.3
6	5.4	5.5	5.2	5.5	5.3	5.5	5.6
9	5.2	5.6	5.6	5.7	5.5	5.4	5.5
Average	5.2	5.3	5.3	5.5	5.3	5.4	5.4
OUTDOOR STORAGE							
3	5.1	5.3	5.3	5.4	5.4	5.6	5.6
6	5.3	5.7	5.7	5.5	5.5	5.6	5.7
9	5.2	5.7	5.8	5.8	5.7	5.6	5.7
Average	5.2	5.6	5.6	5.6	5.5	5.6	5.7

The addition of the clay plus the extra water to maintain the workability approximately the same very slightly increased the absorption. Although not presented in the table, the absorption of the concrete containing No. 2 cement was slightly greater than for the others.

3. RESISTANCE TO FREEZING AND THAWING

The absorption specimens which received the freezing and thawing exposure disintegrated [5] within two years. These cylinders received the same treatment as those subjected to freezing and thawing and later tested in compression, except that they were dried in a gas oven at a temperature of 100° to 130° C. at the ages of 3, 6, and 9 months and 1 year or, roughly, in terms of freezing and thawing, at 40, 100, 150, and 200 cycles. The prime factor was apparently the cement. Those test pieces made with cement No. 1 disintegrated, in general, sooner than the others. No. 3 cement produced the concrete of highest resistance. When the cement was replaced by clay, the table shows that clay No. 2 gave better resistance than the other two clays. In fact, its use distinctly improved the resistance of the concrete made from cements Nos. 1 and 2. The average number of cycles to produce disintegration shown in Table 8 indicate that the concretes containing clay were usually slightly less resistant than the plain concrete, but here again the dispersion of the data was such that too close a comparison is not warranted. Each value in the body of the

[5] A specimen was considered to be disintegrated when 4 or 5 per cent could be broken off with the hands. The disintegration was initially evidenced by crazing.

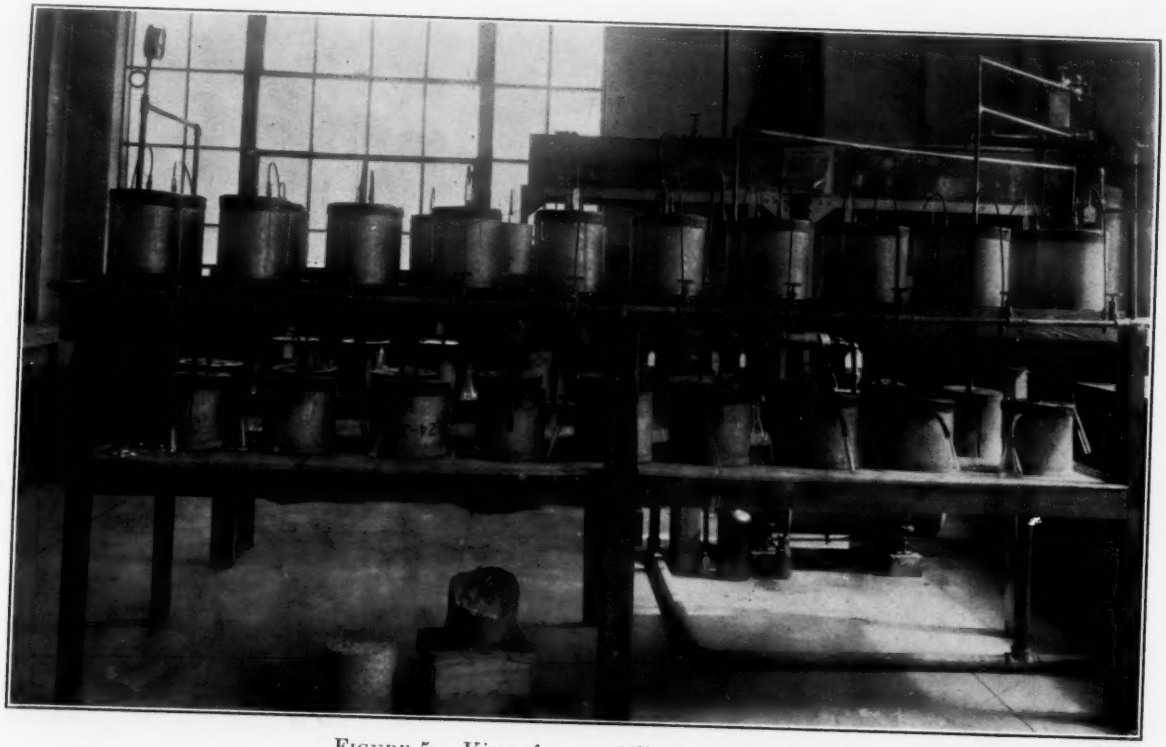


FIGURE 5.—*View of permeability test apparatus*

table is the average for three specimens of the number of freezing and thawing cycles sustained before disintegration.

Cylinders that were kept continually damp showed no ill effects (except in a very few cases) from 400 cycles of freezing and thawing. The compressive strength results obtained with these cylinders also indicated that the freezing and thawing exposure unaccompanied by drying was no more severe than the outdoor exposure.

TABLE 8.—*Freezing and thawing cycles sustained before disintegration*

Cement	I	II			III		
	Plain concrete	10 per cent of cement replaced by clays Nos.—			7½ per cent of sand replaced by clays Nos.—		
		1	2	3	1	2	3
1	170	155	285	150	175	185	175
2	265	200	335	180	220	210	150
3	335	295	335	290	260	295	215
Average	256	217	319	206	218	230	179
General average	256	247			209		

4. PERMEABILITY

It was initially planned to test the permeability specimens over a period of 24 hours at a pressure of 40 pounds per square inch at 3 months age and at 100 pounds per square inch at the later ages. After most of the tests had been completed for the age of 6 months it was quite evident that the results being obtained were of little value because of their extreme variability. At the suggestion of Colonel Cooper a few auxiliary tests were made in which the specimens were kept under water pressure for 12 days. The results indicated that a period of at least two weeks under pressure was necessary to obtain a good picture of the behavior of any specimen. For the retests at age 9 months and later ages this procedure was adopted.

The adoption of the 2-week period of test necessitated an enlargement of the testing apparatus such that 50 specimens could be tested at one time. A view of the apparatus is shown in Figure 5. The freezing and thawing specimens were tested with water surrounding them except for the top 1½ inches. The specimens stored outdoors being initially dry were placed in containers having bottom outlets; the only water present, therefore, was that coming through the specimens. Evaporation losses were minimized, and the entrance of water into the containers from the top of the specimen was prevented by the use of rubber bands encircling the top rim of the container and sealed with paraffin to the top edge of the test piece.

A water pressure of 100 pounds per square inch was maintained by means of compressed air on a tank containing tap water. The variation in pressure during a test rarely exceeded 5 per cent and was usually about 2 per cent.

The rate of leakage of a single specimen or the average for a group of specimens rarely remained the same from day to day. Therefore, the relative permeability of one group of specimens as compared with that for another group is different for one time after the beginning of the test than for another, and consequently a statement of permeability or relative permeability in terms of leakage at a given time

means little unless it is qualified by a description of the trend. This can best be shown by a graphical representation of the average rates of leakage during the periods of test.

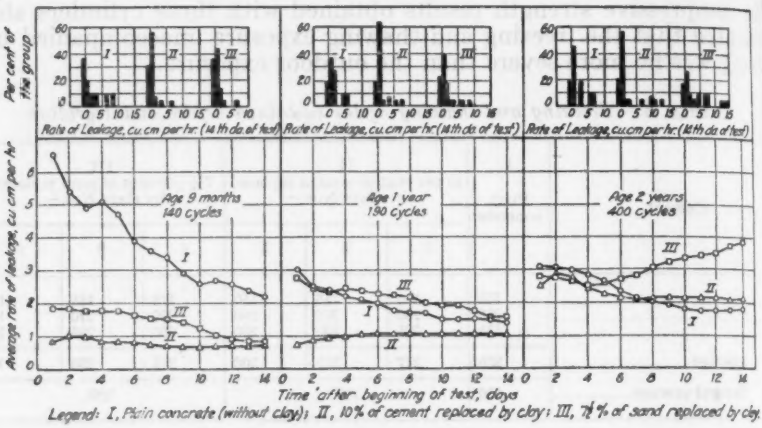

Per cent of the group
Rate of Leakage, cu cm per hr. (14th day of test)
Average rate of leakage, cu cm per hr
Age 9 months 140 cycles
Age 1 year 190 cycles
Age 2 years 400 cycles
Time after beginning of test, days
Legend: I, Plain concrete (without clay); II, 10% of cement replaced by clay; III, 7½% of sand replaced by clay.

FIGURE 6.—*Comparison of permeabilities of concretes I, II, and III after exposure to freezing and thawing*

The average rates of leakage for several groups of specimens are shown by the curves of Figures 6, 7, 8, and 9. In the same figures the frequency distributions of the rates of leakage on the fourteenth day of test are shown by the histograms. The first column on the left of

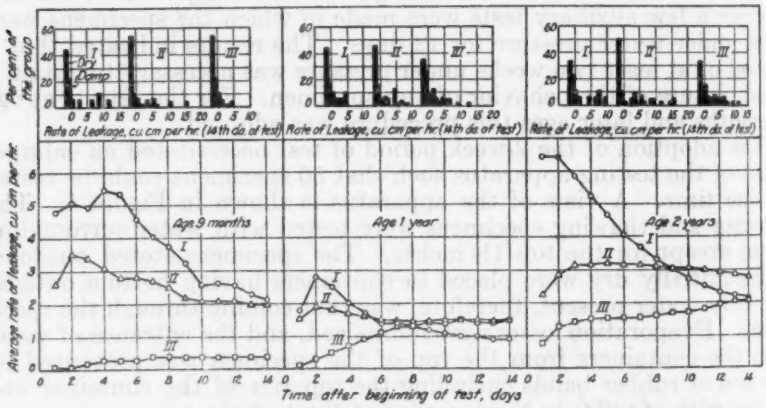

Per cent of the group
Dry
Damp
Rate of Leakage, cu cm per hr. (14th day of test)
Average rate of leakage, cu cm per hr
Age 9 months
Age 1 year
Age 2 years
Time after beginning of test, days

FIGURE 7.—*Comparison of permeabilities of concretes I, II, and III subjected to outdoor exposure*

NOTE.—Of the columns of the histograms to the left, of the abscissa representing zero leakage the one farthest to the left shows the percentage of the group of specimens that were still dry on the outside after 14 days under test and the one nearest the zero abscissa shows the percentage that were damp but not leaking sufficiently to measure.

each of the histograms in Figures 7 and 9, representing specimens of outdoor exposure, indicates the percentage of those of the group that were dry on the outside at the fourteenth day of test. The second column shows the percentage of the total number in a group that were damp, but did not give a measurable amount of leakage.

An inspection of histograms in Figures 6, 7, 8, and 9 will reveal a decidedly skew distribution of rates of leakage. Although the curves in the same figures represent the customary arithmetic mean, it seems that a weighted mean or the median would give a more signi-

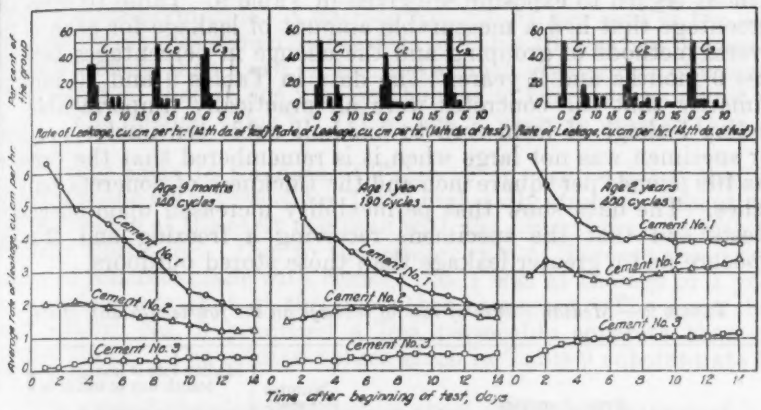

Per cent of the group
Rate of Leakage, cu cm per hr. (14th da of test)
Average rate of leakage, cu cm per hr.
Age 9 months 140 cycles
Age 1 year 190 cycles
Age 2 years 400 cycles
Cement No. 1
Cement No. 2
Cement No. 3
Time after beginning of test, days

FIGURE 8.—*Effect of kind of cement on the permeabilities of the concretes frozen and thawed*

ficant value. The arithmetic mean is greatly affected by the extreme values, and these are the ones in which there is the least confidence, not merely because of the large numerical value but because it is known that there are certain conditions such as undetected injury to

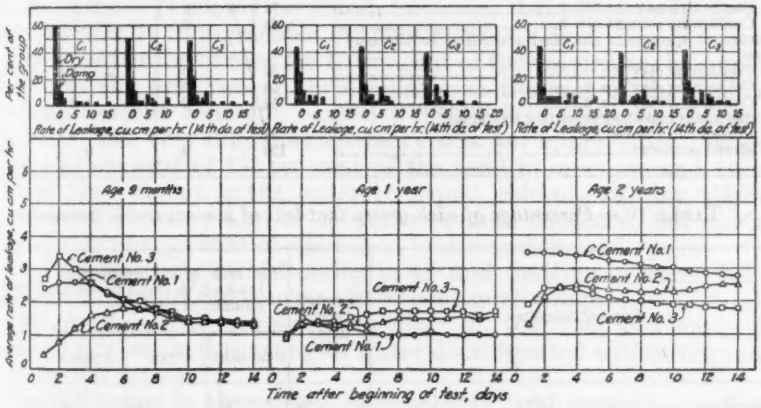

Per cent of the group
Dry
Damp
Rate of Leakage, cu cm per hr. (14th da of test)
Average rate of leakage, cu cm per hr.
Age 9 months
Age 1 year
Age 2 years
Cement No. 1
Cement No. 2
Cement No. 3
Time after beginning of test, days

FIGURE 9.—*Effect of the kind of cement on the permeabilities of the concretes stored outdoors*

NOTE.—Of the columns of the histograms to the left of the abscissa representing zero leakage, the one farthest to the left shows the percentage of the group of specimens that were still dry on the outside after 14 days under test and the one nearest the zero abscissa shows the percentage that were damp but not leaking sufficiently to measure.

the specimen, fluctuation of pressure, etc., which have a tendency to increase leakage.

An illustration of the large effect of extreme values on the arithmetic mean may be had by referring to Figure 7. The average rate of leakage of the 18 specimens of plain concrete, I, age two years on

the second day of test, is 6.4 cm^3 per hour. If the values for two specimens having the greatest leakage were not included, the arithmetic mean for the remaining 16 would be 2.7 cm^3 per hour.

The median values for the several types of concrete when considered without regard to exposure are given in Table 9. Table 10 gives the percentage that had a measurable amount of leakage for each of the several methods of grouping and the change in percentages between ages 9 months and 2 years. The data in Tables 9 and 10 indicate primarily that the concretes were all practically impermeable. A median leakage of from zero to one-half cubic centimeter per hour per specimen was not large when it is remembered that the pressure was 100 pounds per square inch and the thickness of concrete only 3½ inches. The data show that permeability increased upon successive retests and that the specimens receiving a freezing and thawing exposure had a greater leakage than those stored outdoors.

TABLE 9.—*Median values of rate of leakage on the fourteenth day of test*

Type of concrete	Number of specimens	Median rate of leakage on the fourteenth day of test at ages—		
		9 months	1 year	2 years
		cm³/hr.	*cm³/hr.*	*cm³/hr.*
Average of all specimens classified according to per cent of clay:				
I. No clay	29	0	0.1	0.2
II. 10 per cent of cement replaced by clay	81	0	.1	.2
III. 7½ per cent of sand replaced by clay	77	0	.1	.4
Average of all specimens classified according to the cement used:				
Containing cement No. 1	54	0	0	.4
Containing cement No. 2	71	0	.2	.5
Containing cement No. 3	62	0	.1	.2
Average of specimens classified according to the clay used:				
Containing clay No. 1	52	0	.1	.3
Containing clay No. 2	54	0	.1	.2
Containing clay No. 3	52	0	.2	.5
All specimens classified according to storage:				
Frozen and thawed	61	.3	.4	.5
Stored outdoors	126	0	0	0

TABLE 10.—*Percentage of each group that leaked a measurable amount*

Type of concrete	Number of specimens	Per cent of the group that leaked a measurable amount at ages of—			Change in percentage from 9 months to 2 years
		9 months	1 year	2 years	
I. No clay	29	45	55	59	14
II. 10 per cent of cement replaced by clay	81	47	53	54	7
III. 7½ per cent of sand replaced by clay	77	36	51	61	25
Containing cement No. 1	54	35	47	56	21
Containing cement No. 2	71	49	59	63	14
Containing cement No. 3	62	40	52	53	13
Containing clay No. 1	52	42	52	58	16
Containing clay No. 2	54	37	50	57	20
Containing clay No. 3	52	48	54	58	10
Frozen and thawed	61	67	80	82	15
Stored outdoors	126	30	39	46	16

While the median values show that the plain concrete, I, and that with 10 per cent by volume of the cement replaced by clay, II, have the same permeability at all ages tested, the data of Table 10 indicate that initially I was slightly less permeable than II, but having a greater rate of increase in permeability upon retest, it was at age 2 years slightly more permeable. Concrete No. III, 7½ per cent of the sand replaced by clay, as shown by the data of Table 10, was less permeable at age 9 months than I and II, but had a much greater rate of increase upon retest so that at age 2 years the rate of leakage was about the same. The median value for III at age 2 years is greater than for I and II.

Referring again to the data of Table 10, it may be noted that the concrete made with cement No. 1, the high-early strength cement, was less permeable at the early age than with the concretes made with the ordinary Portlands. Due to the greater rate of increase the permeability of concrete made with cement No. 1 was at the age of 2 years midway between that of the two other concretes. The data show that cement No. 3 produced a less permeable concrete than did cement No. 2. The median values given in Table 9 substantiate the conclusions.

In the case of the clays the indices show a slight advantage of Nos. 1 and 2 over No. 3.

VII. CONCLUSIONS

The replacement of 7½ per cent of the volume of the sand by an equal volume of clay increased the compressive strength 1 to 37 per cent. At 9 months the permeability was decreased; later it was increased both actually and relative to that of the plain concrete without clay. It should be noted, however, that all of the concretes were practically impermeable in these tests.

The substitution of clay for 10 per cent of the volume of the cement, except for the first two or three months in the case of the ordinary Portland cement concrete, caused a decrease in strength of 0 to 10 per cent. The very slight permeability was not appreciably changed.

The replacement of 7½ per cent of the sand in one case and 10 per cent of the cement in the other by equal volumes of clay slightly increased the absorption for specimens stored outdoors, but did not appreciably change that of specimens frozen and thawed.

Four hundred cycles of freezing in air and thawing in water did no apparent injury to the concrete kept continually damp.

The concrete that was dried out after 40, 100, 150, and 200 cycles of freezing in air and thawing in water disintegrated within the range of 85 to 400 cycles.

The difference in absorption, permeability, and resistance to freezing and thawing between concretes containing and not containing clay was small.

VIII. ACKNOWLEDGMENTS

It is a pleasure to acknowledge the assistance of several members of the bureau's staff, especially that of C. W. Ross, who made some of the tests of concrete specimens, and of A. U. Theuer, who made the plasticity tests of the clays. The program for the tests was prepared with the assistance of Col. Hugh L. Cooper, and the work was carried on jointly by the Hugh L. Cooper Co. and the Bureau of Standards.

WASHINGTON, December 15, 1932.

REFERENCE TABLES FOR PLATINUM TO PLATINUM-RHODIUM THERMOCOUPLES

By Wm. F. Roeser and H. T. Wensel

ABSTRACT

Reference tables for use with platinum to platinum-10 per cent rhodium and platinum to platinum-13 per cent rhodium thermocouples have been prepared. When these tables are used, the deviation curves obtained for individual couples, have no points of inflection and are, with few exceptions, linear. These tables are based on the International Temperature Scale, so that the indications of a thermocouple whose calibration is obtained by extrapolation of a deviation curve above the gold point will agree in this region with those of an optical pyrometer.

CONTENTS

		Page
I.	Introduction	275
II.	Experimental procedure	276
III.	Construction of table	277
IV.	Results	278
V.	Summary	279

I. INTRODUCTION

Although the platinum to platinum-10 per cent rhodium thermocouple is used to define the Interanational Temperature Scale only in the range 660° to 1,063° C., this couple, as well as the 13 per cent rhodium couple, is used extensively in measuring temperatures in the range 0° to 1,500° C. Convenient and reliable means are required not only for calibrating these couples over this entire range but also for reducing readings of electromotive force to temperature.

Since the platinum resistance thermometer, in the range 0° to 660° C., and the optical pyrometer, in the range above 1,063° C., are also used in defining the International Temperature Scale, it is necessary to compare thermocouples either directly or indirectly with these instruments in their respective temperature ranges. Since it is not convenient to compare thermocouples directly with the other types of instruments, it is necessary to resort to indirect methods.

The indirect comparison of thermocouples with resistance thermometers in the range 0° to 660° C. is easily carried out by employing thermometric fixed points defined by the temperature of equilibrium between the solid and liquid phases or the liquid and vapor phases of pure substances. There are a large number of such points in this temperature range. However, there are no metals having freezing points above the freezing point of copper (1,083° C.) with which conveniently to compare thermocouples and optical pyrometers. The freezing points of nickel (1,455° C.) and of palladium (1,555° C.) are near the upper useful limit of thermocouples, but both of these materials should be melted in vacuo to obtain the best results. It is therefore desirable in the routine calibration of thermocouples (ex-

cepting those cases where the highest possible accuracy is required) to employ a method which does not require the comparison of each thermocouple with the optical pyrometer.

The method of calibration employing standard reference tables with suitable deviation curves has been described by Sosman [1] and Adams.[2] As pointed out by these authors such reference curves are arbitrary but it is advisable, for the sake of accuracy, that they represent closely the actual form of the curve. If the reference table is properly constructed, the deviations of thermocouple calibrations from it will be small and the resulting deviation curve approximately linear, requiring comparatively few calibrations points to fix the curve.

Standard reference tables for use with platinum to platinum-10 per cent rhodium thermocouples are given by Sosman and by Adams in the references cited. The table given by Sosman is based upon the measurements made by Day and Sosman [3] with the gas thermometer and thermocouples. The table given by Adams is essentially the same as that of Sosman above 650° C., but the values below 650° C. have been altered to agree with changes in the temperature scale.

The adoption of the International Temperature Scale [4] defining temperatures above 1,063° C. in terms of Wien's law of radiation, with an assigned value of C_2, raises the question as to whether, in this region, Adams's reference table represents the emf temperature relation on the international scale. Measurements at the Bureau of Standards [5] of the temperatures on the international scale of several of the fixed points used by Day and Sosman have indicated fairly well the differences between this scale and that used by Day and Sosman. If it be taken for granted that the thermocouples used by these authors have the same characteristics as those now being used, the table of Adams may be modified by merely converting the temperatures in this table, above 1,063° C., to the international scale by applying the differences deduced. It seemed advisable, however, to adopt the sounder procedure of comparing the indications of thermocouples with those of the optical pyrometer above 1,063° C. and with those of platinum resistance thermometers in the range below 660° C.

II. EXPERIMENTAL PROCEDURE

Twenty standard thermocouples, platinum to platinum-10 per cent rhodium, from four different manufacturers were calibrated in the range 660° to 1,063° C. in accordance with the procedure specified for the International Temperature Scale. They were then calibrated in the range 0° to 420° C. at four thermometric fixed points which had been previously determined by the platinum resistance thermometer. Above 1,063° C. eight of the thermocouples were directly compared with an optical pyrometer by employing an electrically heated black body up to 1,450° C. The thermocouples were then heated until the platinum at the hot junction melted and the emf observed at the instant of melting was assigned to the temperature previously determined for the platinum point, 1,773° C.[6]

---

[1] Am. J. Sci. (4), vol. *30*, p. 7, 1910.
[2] J. Am. Chem. Soc., vol. *36*, p. 65, 1914, Pyrometry Symposium. A. I. M. M. E., p. 165, 1919.
[3] Car. Inst. of Wash. Pub. No. 157, 1911. Am. J. Sci., vol. 33, p. 517, 1912.
[4] Proc. Seventh General Conference of Weights and Measures. 1927, p. 56. Text in Annex IV, p. 94. G. K. Burgess, B. S. Jour. Research, vol. 1, p. 635, 1928.
[5] B. S. Jour. Research, vol. 5, p. 1309, 1930.
[6] B. S. Jour. Research, vol. 6, p. 1119, 1931.

III. CONSTRUCTION OF TABLE

The alloy element of the standard platinum-rhodium thermocouple is specified as that alloy which develops between 10.2 and 10.4 mv against pure platinum at the gold point. This fixes the rhodium content of the alloy at 10 per cent as accurately as can be done by chemical analysis. Since the value given in Adams's table at the gold point (10.301 mv) is near the mean of these limits it was considered advisable to retain this value in the new table.

Since the average emf of the couples investigated differed by ΔE (about 4 μv) from Adams's table at the gold point, the emf at each calibration point was increased by an amount $\frac{E \text{ at calibration point}}{10{,}301} \times \Delta E$.

This yielded a skeleton table, given in Table 1, which agrees with Adams's table at the gold point and from which nearly all the thermocouples deviated linearly. The few deviation curves which were not straight lines contained no points of inflection. Typical deviation curves from Adams's table and this skeleton table are shown in Figure 1.

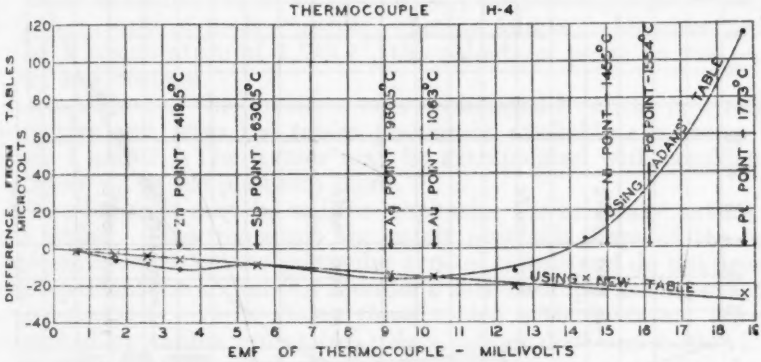


FIGURE 1.—*Deviation curves of a typical 10 per cent rhodium thermocouple*

Several equations were used for interpolating between the values in the skeleton table, since no simple equation was found which would fit the values over the entire temperature range. In order to make the curve and its first derivative continuous, the slopes of each pair of successive interpolation equations were made equal at the point in common. These equations are also given in Table 1.

TABLE 1.—*Calibration points and derived emf's*

	Temperature	Emf
	° C.	μv
Melting point of ice	0.0	0
Boiling point of water	100.0	643
Freezing point of tin	231.9	1,709
Freezing point of lead	327.4	2,567
Freezing point of zinc	419.45	3,436
Freezing point of antimony	630.5	5,535
Freezing point of silver	960.5	9,117
Freezing point of gold	1,063.0	10,301
	1,250	12,522
	1,400	14,312
Melting point of platinum	1,773	18,690

Equations used for interpolating between calibration points

0° to 231.9° C.,	$E=5.45018t$	$+0.0109517t^2$	$-0.0000115353t^3$	
231.9° to 327.4° C.,	$E=-35.01$	$+6.10222t$	$+0.00728131t^2$	$-0.00000502491t^3$
327.4° to 419.45° C.,	$E=-5375$	$+6.29745t$	$+0.00661301t^2$	$-0.00000427121t^3$
419.45° to 630.5° C.,	$E=-309.17$	$+8.29558t$	$+0.00144103t^2$	$+0.00000016341t^3$
630.5° to 660° C.,	$E=-263.93$	$+8.04427t$	$+0.00189675t^2$	$-0.00000010773t^3$
660° to 1,063° C.,	$E=-333.29$	$+8.29175t$	$+0.00161080t^2$	
1,063° to 1,250° C.,	$E=1,858.96$	$+1.76577t$	$+0.00807342t^2$	$-0.00000212935t^3$
1,250° to 1,773° C.,	$E=-2,074.00$	$+10.86774t$	$+0.00106153t^2$	$-0.00000033143t^3$

A table of approximate values for platinum to platinum-13 per cent rhodium thermocouples is given in Bureau of Standards Technologic Paper No. 170. This table was determined before the adoption of the International Temperature Scale, and is subject to the same disadvantages as Adams' table for the 10 per cent rhodium thermocouples. A typical deviation curve from this table is shown in Figure 2.

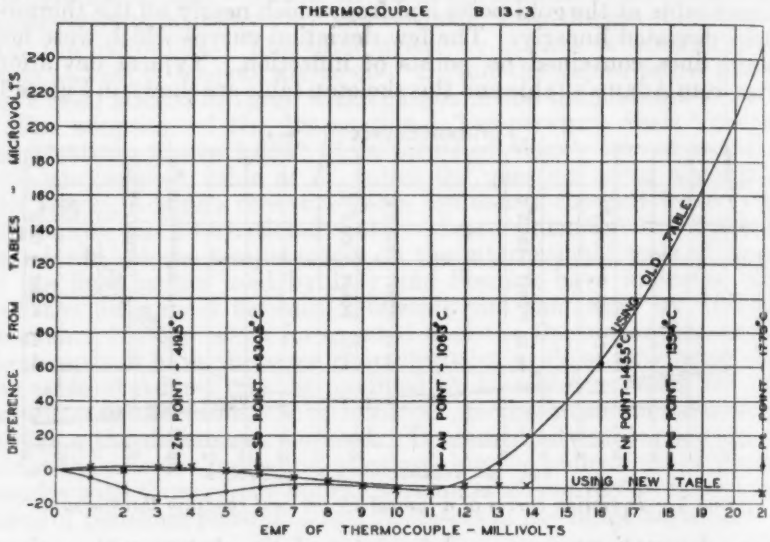


FIGURE 2.—*Deviation curves of a typical 13 per cent rhodium thermocouple*

A new reference table for 13 per cent rhodium thermocouples was obtained by comparing four such couples with 10 per cent rhodium couples and by applying the difference between the two types to the tabular values for 10 per cent rhodium couples.

IV. RESULTS

Corresponding values of emf and temperature, as derived in this work for the 10 and 13 per cent rhodium thermocouples, are given in Tables 2 to 5. Below 1,200° C. the maximum difference between Table 2 and Adams' table is 0.7° C.

Previous to this the best working tables available for the temperature emf relations of platinum to platinum rhodium thermocouples were those on pages 306 and 308 (Adams' table) of Bureau of Standards Technologic Paper No. 170, and the bureau has, in the past, recommended their use. Recent progress in optical pyrometry and the adoption of the International Temperature Scale have indicated the desirability of reference tables which represent more accurately the characteristics of these couples. The publication of these tables, however, should not be construed as indicating in any way a change in the characteristics of the couples.

The values in these reference tables above the gold point are practically identical up to the palladium point (1,555° C.) with those which would have been obtained by simply converting the temperatures in the old tables to the international scale by means of the differences between the scales inferred from recent determinations of fixed points. This indicates that the thermocouples used by Day and Sosman had essentially the same characteristics as those now being used. As an illustration the emf of the 10 per cent rhodium couple was found to be 16.136 mv at 1,553.6° C., the freezing point of palladium, from optical measurements, whereas Adams' table gives 16.14 mv for a temperature of 1,549.2°, the palladium point on the scale of Day and Sosman.

A comparison of the deviation curves obtained from the new reference tables and from the tables previously available are shown in Figures 1 and 2. The former may be extrapolated with confidence practically up to the platinum point.

In conclusion it may be well to emphasize the arbitrary nature of these tables. They represent accurately only the shape of the emf temperature curve for the particular type of couple and do not necessarily represent the actual emf even for a thermocouple having exactly the composition given. Using these tables with deviation curves determined by calibration at two points (about 600° and 1,200° C.), a calibration is obtained which is not in error by more than 3° C. from 0° to 1,500° C.

V. SUMMARY

Reference tables for two classes of platinum-rhodium thermocouples, the 10 per cent and 13 per cent rhodium alloys versus platinum have been determined. They accurately represent the shape of the emf temperature curves for these couples when the International Temperature Scale is used. The deviation from these tables of the couples now being used show no points of inflection and with few exceptions, are linear.

TABLE 2.—*Reference table for Pt to Pt–10 per cent Rh thermocouple*

[Emfs are expressed in microvolts and temperatures in °C. Cold junctions at 0° C.]

E Microvolts	0	1,000	2,000	3,000	4,000	5,000	6,000	7,000	8,000	E Microvolts
0	0	146.9	265.0	373.7	477.7	578.1	675.3	769.5	861.0	0
	17.7	*12.5*	*11.2*	*10.5*	*10.2*	*9.9*	*9.5*	*9.3*	*9.0*	
100	17.7	159.4	276.2	384.2	487.9	588.0	684.8	778.8	870.0	100
	16.7	*12.3*	*11.1*	*10.5*	*10.2*	*9.8*	*9.5*	*9.2*	*9.0*	
200	34.4	171.7	287.3	394.7	498.1	597.8	694.3	788.0	879.0	200
	15.8	*12.1*	*11.0*	*10.5*	*10.1*	*9.8*	*9.5*	*9.2*	*9.0*	
300	50.2	183.8	298.3	405.2	508.2	607.6	703.8	797.2	888.0	300
	15.2	*12.0*	*11.0*	*10.5*	*10.1*	*9.8*	*9.5*	*9.2*	*9.0*	
400	65.4	195.8	309.3	415.7	518.3	617.4	713.3	806.4	897.0	400
	14.6	*11.8*	*10.9*	*10.4*	*10.1*	*9.7*	*9.4*	*9.2*	*8.9*	
500	80.0	207.6	320.2	426.1	528.4	627.1	722.7	815.6	905.9	500
	14.1	*11.7*	*10.8*	*10.4*	*10.0*	*9.7*	*9.4*	*9.1*	*8.9*	
600	94.1	219.3	331.0	436.5	538.4	636.8	732.1	824.7	914.8	600
	13.7	*11.6*	*10.7*	*10.3*	*10.0*	*9.7*	*9.4*	*9.1*	*8.9*	
700	107.8	230.9	341.7	446.8	548.4	646.5	741.5	833.8	923.7	700
	13.3	*11.5*	*10.7*	*10.3*	*9.9*	*9.6*	*9.4*	*9.1*	*8.9*	
800	121.1	242.4	352.4	457.1	558.3	656.1	750.9	842.9	932.6	800
	13.0	*11.3*	*10.7*	*10.3*	*9.9*	*9.6*	*9.3*	*9.1*	*8.8*	
900	134.1	253.7	363.1	467.4	568.2	665.7	760.2	852.0	941.4	900
	12.8	*11.3*	*10.6*	*10.3*	*9.9*	*9.6*	*9.3*	*9.0*	*8.8*	
1,000	146.9	265.0	373.7	477.7	578.1	675.3	769.5	861.0	950.2	1,000

E Microvolts	9,000	10,000	11,000	12,000	13,000	14,000	15,000	16,000	17,000	E Microvolts
0	950. 2	1, 037. 2	1, 122. 3	1, 206. 4	1, 290. 0	1, 373. 8	1, 458. 0	1, 542. 6	1, 627. 8	0
	8. 8	8. 6	8. 5	8. 3	8. 3	8. 4	8. 4	8. 5	8. 6	
100	959. 0	1, 045. 8	1, 130. 8	1, 214. 7	1, 298. 3	1, 382. 2	1, 466. 4	1, 551. 1	1, 636. 4	100
	8. 8	8. 6	8. 4	8. 4	8. 4	8. 4	8. 4	8. 5	8. 5	
200	967. 8	1, 054. 4	1, 139. 2	1, 223. 1	1, 306. 7	1, 390. 6	1, 474. 8	1, 559. 6	1, 644. 9	200
	8. 7	8. 5	8. 4	8. 3	8. 4	8. 4	8. 5	8. 5	8. 6	
300	976. 5	1, 062. 9	1, 147. 6	1, 231. 4	1, 315. 1	1, 399. 0	1, 483. 3	1, 568. 1	1, 653. 5	300
	8. 8	8. 6	8. 4	8. 4	8. 4	8. 4	8. 5	8. 5	8. 6	
400	985. 3	1, 071. 5	1, 156. 0	1, 239. 8	1, 323. 5	1, 407. 4	1, 491. 8	1, 576. 6	1, 662. 1	400
	8. 7	8. 5	8. 4	8. 4	8. 3	8. 4	8. 4	8. 5	8. 6	
500	994. 0	1, 080. 0	1, 164. 4	1, 248. 2	1, 331. 8	1, 415. 8	1, 500. 2	1, 585. 1	1, 670. 7	500
	8. 7	8. 5	8. 4	8. 3	8. 4	8. 4	8. 5	8. 6	8. 6	
600	1, 002. 7	1, 088. 5	1, 172. 8	1, 256. 5	1, 340. 2	1, 424. 2	1, 508. 7	1, 593. 7	1, 679. 3	600
	8. 6	8. 5	8. 4	8. 4	8. 4	8. 5	8. 5	8. 5	8. 6	
700	1, 011. 3	1, 097. 0	1, 181. 2	1, 264. 9	1, 348. 6	1, 432. 7	1, 517. 2	1, 602. 2	1, 687. 9	700
	8. 7	8. 4	8. 4	8. 3	8. 4	8. 4	8. 4	8. 5	8. 6	
800	1, 020. 0	1, 105. 4	1, 189. 6	1, 273. 2	1, 357. 0	1, 441. 1	1, 525. 6	1, 610. 7	1, 696. 5	800
	8. 6	8. 5	8. 4	8. 4	8. 4	8. 4	8. 5	8. 6	8. 6	
900	1, 028. 6	1, 113. 9	1, 198. 0	1, 281. 6	1, 365. 4	1, 449. 5	1, 534. 1	1, 619. 3	1, 705. 1	900
	8. 6	8. 4	8. 4	8. 4	8. 4	8. 5	8. 5	8. 5	8. 6	
1,000	1, 037. 2	1, 122. 3	1, 206. 4	1, 290. 0	1, 373. 8	1, 458. 0	1, 542. 6	1, 627. 8	1, 713. 7	1,000

TABLE 3.—*Reference table for Pt to Pt–13 per cent Rh thermocouple*

[Emfs are expressed in microvolts and temperatures in °C. Cold junctions at 0° C.]

E Microvolts	0	1,000	2,000	3,000	4,000	5,000	6,000	7,000	8,000	9,000	E Microvolts
0	0	145.3	258.8	361.0	457.4	549.8	638.3	723.5	806.0	886.1	0
	17.9	*12.2*	*10.6*	*9.9*	*9.5*	*9.0*	*8.7*	*8.4*	*8.1*	*7.9*	
100	17.9	157.5	269.4	370.9	466.9	558.8	647.0	731.9	814.1	894.0	100
	16.7	*12.0*	*10.5*	*9.8*	*9.4*	*9.0*	*8.6*	*8.4*	*8.1*	*7.8*	
200	34.6	169.5	279.9	380.7	476.3	567.8	655.6	740.3	822.2	901.8	200
	15.8	*11.7*	*10.4*	*9.8*	*9.4*	*9.0*	*8.6*	*8.3*	*8.1*	*7.9*	
300	50.4	181.2	290.3	390.5	485.7	576.8	664.2	748.6	830.3	909.7	300
	15.1	*11.5*	*10.3*	*9.7*	*9.3*	*8.9*	*8.6*	*8.3*	*8.0*	*7.8*	
400	65.5	192.7	300.6	400.2	495.0	585.7	672.8	756.9	838.3	917.5	400
	14.5	*11.4*	*10.2*	*9.7*	*9.3*	*8.9*	*8.5*	*8.2*	*8.0*	*7.8*	
500	80.0	204.1	310.8	409.9	504.3	594.6	681.3	765.1	846.3	925.3	500
	13.9	*11.2*	*10.2*	*9.6*	*9.2*	*8.8*	*8.5*	*8.2*	*8.0*	*7.8*	
600	93.9	215.3	321.0	419.5	513.5	603.4	689.8	773.3	854.3	933.1	600
	13.4	*11.1*	*10.1*	*9.5*	*9.1*	*8.8*	*8.5*	*8.2*	*8.0*	*7.8*	
700	107.3	226.4	331.1	429.0	522.6	612.2	698.3	781.5	862.3	940.9	700
	13.0	*10.9*	*10.0*	*9.5*	*9.1*	*8.7*	*8.4*	*8.2*	*8.0*	*7.8*	
800	120.3	237.3	341.1	438.5	531.7	620.9	706.7	789.7	870.3	948.7	800
	12.6	*10.8*	*10.0*	*9.5*	*9.1*	*8.7*	*8.4*	*8.1*	*7.9*	*7.7*	
900	132.9	248.1	351.1	448.0	540.8	629.6	715.1	797.8	878.2	956.4	900
	12.4	*10.7*	*9.9*	*9.4*	*9.0*	*8.7*	*8.4*	*8.2*	*7.9*	*7.7*	
1,000	145.3	258.8	361.0	457.4	549.8	638.3	723.5	806.0	886.1	964.1	1,000

E Microvolts	10,000	11,000	12,000	13,000	14,000	15,000	16,000	17,000	18,000	19,000	E Microvolts
0	964.1	1,040.0	1,113.9	1,186.9	1,259.3	1,331.8	1,404.3	1,476.9	1,550.0	1,623.6	0
	7.6	7.4	7.3	7.2	7.3	7.2	7.3	7.3	7.4	7.4	
100	971.7	1,047.4	1,121.2	1,194.1	1,266.6	1,339.0	1,411.6	1,484.2	1,557.4	1,631.0	100
	7.7	7.5	7.4	7.3	7.2	7.2	7.3	7.3	7.4	7.4	
200	979.4	1,054.9	1,128.6	1,201.4	1,273.8	1,346.2	1,418.9	1,491.5	1,564.8	1,638.4	200
	7.6	7.4	7.3	7.3	7.3	7.3	7.2	7.3	7.3	7.4	
300	987.0	1,062.3	1,135.9	1,208.7	1,281.1	1,353.5	1,426.1	1,498.8	1,572.1	1,645.8	300
	7.7	7.4	7.3	7.2	7.2	7.3	7.2	7.3	7.4	7.4	
400	994.7	1,069.7	1,143.2	1,215.9	1,288.3	1,360.8	1,433.3	1,506.1	1,579.5	1,653.2	400
	7.6	7.4	7.3	7.3	7.2	7.2	7.2	7.3	7.3	7.4	
500	1,002.3	1,077.1	1,150.5	1,223.2	1,295.5	1,368.0	1,440.5	1,513.4	1,586.8	1,660.6	500
	7.6	7.3	7.3	7.2	7.2	7.3	7.3	7.3	7.4	7.4	
600	1,009.9	1,084.4	1,157.8	1,230.4	1,302.7	1,375.3	1,447.8	1,520.7	1,594.2	1,668.0	600
	7.6	7.4	7.3	7.2	7.2	7.3	7.2	7.3	7.3	7.4	
700	1,017.5	1,091.8	1,165.1	1,237.6	1,309.9	1,382.6	1,455.0	1,528.0	1,601.5	1,675.4	700
	7.5	7.4	7.2	7.2	7.3	7.2	7.3	7.3	7.4	7.4	
800	1,025.0	1,099.2	1,172.3	1,244.8	1,317.2	1,389.8	1,462.3	1,535.3	1,608.9	1,682.8	800
	7.5	7.3	7.3	7.3	7.3	7.3	7.3	7.4	7.3	7.4	
900	1,032.5	1,106.5	1,179.6	1,252.1	1,324.5	1,397.1	1,469.6	1,542.7	1,616.2	1,690.2	900
	7.5	7.4	7.3	7.2	7.3	7.2	7.3	7.3	7.4	7.4	
1,000	1,040.0	1,113.9	1,186.9	1,259.3	1,331.8	1,404.3	1,476.9	1,550.0	1,623.6	1,697.6	1,000

TABLE 4.—*Reference table for Pt to Pt–10 per cent Rh thermocouple*

[Emfs are expressed in microvolts and temperatures in °F. Cold junctions at 32 °F.]

E Microvolts	0	1,000	2,000	3,000	4,000	5,000	6,000	7,000	8,000	E Microvolts
0	32. 0	296. 4	509. 0	704. 7	891. 9	1, 072. 6	1, 247. 5	1, 417. 1	1, 581. 8	0
	31. 9	*22. 5*	*20. 1*	*19. 0*	*18. 4*	*17. 7*	*17. 1*	*16. 7*	*16. 2*	
100	63. 9	318. 9	529. 1	723. 7	910. 3	1, 090. 3	1, 264. 6	1, 433. 8	1, 598. 0	100
	30. 0	*22. 1*	*20. 0*	*18. 9*	*18. 3*	*17. 7*	*17. 1*	*16. 6*	*16. 2*	
200	93. 9	341. 0	549. 1	742. 6	928. 6	1, 108. 0	1, 281. 7	1, 450. 4	1, 614. 2	200
	28. 5	*21. 8*	*19. 9*	*18. 8*	*18. 2*	*17. 7*	*17. 1*	*16. 6*	*16. 2*	
300	122. 4	362. 8	569. 0	761. 4	946. 8	1, 125. 7	1, 298. 8	1, 467. 0	1, 630. 4	300
	27. 3	*21. 6*	*19. 8*	*18. 8*	*18. 1*	*17. 6*	*17. 1*	*16. 5*	*16. 1*	
400	149. 7	384. 4	588. 8	780. 2	964. 9	1, 143. 3	1, 315. 9	1, 483. 5	1, 646. 5	400
	26. 3	*21. 3*	*19. 6*	*18. 8*	*18. 1*	*17. 5*	*17. 0*	*16. 5*	*16. 1*	
500	176. 0	405. 7	608. 4	799. 0	983. 0	1, 160. 8	1, 332. 9	1, 500. 0	1, 662. 6	500
	25. 4	*21. 0*	*19. 4*	*18. 7*	*18. 1*	*17. 5*	*16. 9*	*16. 5*	*16. 0*	
600	201. 4	426. 7	627. 8	817. 7	1, 001. 1	1, 178. 3	1, 349. 8	1, 516. 5	1, 678. 6	600
	24. 6	*20. 9*	*19. 3*	*18. 6*	*18. 0*	*17. 4*	*16. 9*	*16. 4*	*16. 0*	
700	226. 0	447. 6	647. 1	836. 3	1, 019. 1	1, 195. 7	1, 366. 7	1, 532. 9	1, 694. 6	700
	24. 0	*20. 7*	*19. 3*	*18. 5*	*17. 9*	*17. 3*	*16. 9*	*16. 3*	*16. 0*	
800	250. 0	468. 3	666. 4	854. 8	1, 037. 0	1, 213. 0	1, 383. 6	1, 549. 2	1, 710. 6	800
	23. 4	*20. 4*	*19. 2*	*18. 6*	*17. 8*	*17. 3*	*16. 8*	*16. 3*	*15. 9*	
900	273. 4	488. 7	685. 6	873. 4	1, 054. 8	1, 230. 3	1, 400. 4	1, 565. 5	1, 726. 5	900
	23. 0	*20. 3*	*19. 1*	*18. 5*	*17. 8*	*17. 2*	*16. 7*	*16. 3*	*15. 9*	
1, 000	296. 4	509. 0	704. 7	891. 9	1, 072. 6	1, 247. 5	1, 417. 1	1, 581. 8	1, 742. 4	1, 000

E Microvolts	9,000	10,000	11,000	12,000	13,000	14,000	15,000	16,000	17,000	E Microvolts
0	1, 742. 4	1, 899. 0	2, 052. 1	2, 203. 5	2, 354. 0	2, 504. 8	2, 656. 4	2, 808. 7	2, 962. 0	0
	15. 8	*15. 5*	*15. 2*	*15. 0*	*15. 0*	*15. 2*	*15. 1*	*15. 3*	*15. 4*	
100	1, 758. 2	1, 914. 5	2, 067. 3	2, 218. 5	2, 369. 0	2, 520. 0	2, 671. 5	2, 824. 0	2, 977. 4	100
	15. 8	*15. 4*	*15. 2*	*15. 0*	*15. 1*	*15. 1*	*15. 2*	*15. 3*	*15. 4*	
200	1, 774. 0	1, 929. 9	2, 082. 5	2, 233. 5	2, 384. 1	2, 535. 1	2, 686. 7	2, 839. 3	2, 992. 8	200
	15. 7	*15. 4*	*15. 2*	*15. 0*	*15. 1*	*15. 1*	*15. 2*	*15. 3*	*15. 5*	
300	1, 789. 7	1, 945. 3	2, 097. 7	2, 248. 5	2, 399. 2	2, 550. 2	2, 701. 9	2, 854. 6	3, 008. 3	300
	15. 8	*15. 4*	*15. 1*	*15. 1*	*15. 1*	*15. 1*	*15. 3*	*15. 3*	*15. 5*	
400	1, 805. 5	1, 960. 7	2, 112. 8	2, 263. 6	2, 414. 3	2, 565. 3	2, 717. 2	2, 869. 9	3, 023. 8	400
	15. 7	*15. 3*	*15. 1*	*15. 1*	*15. 0*	*15. 1*	*15. 2*	*15. 3*	*15. 5*	
500	1, 821. 2	1, 976. 0	2, 127. 9	2, 278. 7	2, 429. 3	2, 580. 4	2, 732. 4	2, 885. 2	3, 039. 3	500
	15. 6	*15. 3*	*15. 1*	*15. 0*	*15. 1*	*15. 2*	*15. 3*	*15. 4*	*15. 4*	
600	1, 836. 8	1, 991. 3	2, 143. 0	2, 293. 7	2, 444. 4	2, 595. 6	2, 747. 7	2, 900. 6	3, 054. 7	600
	15. 6	*15. 2*	*15. 2*	*15. 1*	*15. 1*	*15. 2*	*15. 3*	*15. 4*	*15. 5*	
700	1, 852. 4	2, 006. 5	2, 158. 2	2, 308. 8	2, 459. 5	2, 610. 8	2, 763. 0	2, 916. 0	3, 070. 2	700
	15. 6	*15. 2*	*15. 1*	*15. 0*	*15. 1*	*15. 2*	*15. 2*	*15. 3*	*15. 5*	
800	1, 868. 0	2, 021. 7	2, 173. 3	2, 323. 8	2, 474. 6	2, 626. 0	2, 778. 2	2, 931. 3	3, 085. 7	800
	15. 5	*15. 2*	*15. 1*	*15. 1*	*15. 1*	*15. 2*	*15. 2*	*15. 4*	*15. 5*	
900	1, 883. 5	2, 036. 9	2, 188. 4	2, 338. 9	2, 489. 7	2, 641. 2	2, 793. 4	2, 946. 7	3, 101. 2	900
	15. 5	*15. 2*	*15. 1*	*15. 1*	*15. 1*	*15. 2*	*15. 3*	*15. 3*	*15. 5*	
1, 000	1, 899. 0	2, 052. 1	2, 203. 5	2, 354. 0	2, 504. 8	2, 656. 4	2, 808. 7	2, 962. 0	3, 116. 7	1, 000

TABLE 5.—*Reference table for Pt to Pt–13 per cent Rh thermocouple*

[Emfs are expressed in microvolts and temperatures in °F. Cold junctions at 32° F.]

E Microvolts	0	1,000	2,000	3,000	4,000	5,000	6,000	7,000	8,000	9,000	E Microvolts
0	32. 0	293. 5	497. 8	681. 8	855. 3	1, 021. 6	1, 180. 9	1, 334. 3	1, 482. 8	1, 627. 0	0
	32. 2	*22. 0*	*19. 1*	*17. 8*	*17. 0*	*16. 2*	*15. 6*	*15. 1*	*14. 6*	*14. 2*	
100	64. 2	315. 5	516. 9	699. 6	872. 3	1, 037. 8	1, 196. 5	1, 349. 4	1, 497. 4	1, 641. 2	100
	30. 1	*21. 6*	*18. 9*	*17. 7*	*17. 0*	*16. 2*	*15. 6*	*15. 1*	*14. 6*	*14. 1*	
200	94. 3	337. 1	535. 8	717. 3	889. 3	1, 054. 0	1, 212. 1	1, 364. 5	1, 512. 0	1, 655. 3	200
	28. 4	*21. 1*	*18. 7*	*17. 6*	*16. 9*	*16. 2*	*15. 5*	*15. 0*	*14. 5*	*14. 1*	
300	122. 7	358. 2	554. 5	734. 9	906. 2	1, 070. 2	1, 227. 6	1, 379. 5	1, 526. 5	1, 669. 4	300
	27. 2	*20. 7*	*18. 6*	*17. 5*	*16. 8*	*16. 1*	*15. 4*	*14. 9*	*14. 4*	*14. 1*	
400	149. 9	378. 9	573. 1	752. 4	923. 0	1, 086. 3	1, 243. 0	1, 394. 4	1, 540. 9	1, 683. 5	400
	26. 1	*20. 4*	*18. 4*	*17. 4*	*16. 7*	*16. 0*	*15. 3*	*14. 8*	*14. 4*	*14. 0*	
500	176. 0	399. 3	591. 5	769. 8	939. 7	1, 102. 3	1, 258. 3	1, 409. 2	1, 555. 3	1, 697. 5	500
	25. 0	*20. 2*	*18. 3*	*17. 3*	*16. 6*	*15. 9*	*15. 3*	*14. 8*	*14. 4*	*14. 1*	
600	201. 0	419. 5	609. 8	787. 1	956. 3	1, 118. 2	1, 273. 6	1, 424. 0	1, 569. 7	1, 711. 6	600
	24. 1	*20. 0*	*18. 2*	*17. 2*	*16. 4*	*15. 8*	*15. 3*	*14. 8*	*14. 4*	*14. 0*	
700	225. 1	439. 5	628. 0	804. 3	972. 7	1, 134. 0	1, 288. 9	1, 438. 8	1, 584. 1	1, 725. 6	700
	23. 4	*19. 7*	*18. 0*	*17. 1*	*16. 4*	*15. 7*	*15. 2*	*14. 7*	*14. 4*	*14. 0*	
800	248. 5	459. 2	646. 0	821. 4	989. 1	1, 149. 7	1, 304. 1	1, 453. 5	1, 598. 5	1, 739. 6	800
	22. 7	*19. 4*	*18. 0*	*17. 0*	*16. 3*	*15. 6*	*15. 1*	*14. 6*	*14. 3*	*13. 9*	
900	271. 2	478. 6	664. 0	838. 4	1, 005. 4	1, 165. 3	1, 319. 2	1, 468. 1	1, 612. 8	1, 753. 5	900
	22. 3	*19. 2*	*17. 8*	*16. 9*	*16. 2*	*15. 6*	*15. 1*	*14. 7*	*14. 2*	*13. 9*	
1,000	293. 5	497. 8	681. 8	855. 3	1, 021. 6	1, 180. 9	1, 334. 3	1, 482. 8	1, 627. 0	1, 767. 4	1,000

E Microvolts	10,000	11,000	12,000	13,000	14,000	15,000	16,000	17,000	18,000	19,000	E Microvolts
0	1, 767. 4	1, 904. 0	2, 037. 0	2, 168. 4	2, 298. 7	2, 429. 2	2, 559. 7	2, 690. 4	2, 822. 0	2, 954. 5	0
	13. 8	*13. 4*	*13. 2*	*13. 0*	*13. 1*	*13. 0*	*13. 1*	*13. 2*	*13. 3*	*13. 3*	
100	1, 781. 2	1, 917. 4	2, 050. 2	2, 181. 4	2, 311. 8	2, 442. 2	2, 572. 8	2, 703. 6	2, 835. 3	2, 967. 8	100
	13. 7	*13. 4*	*13. 2*	*13. 1*	*13. 0*	*13. 0*	*13. 1*	*13. 1*	*13. 3*	*13. 3*	
200	1, 794. 9	1, 930. 8	2, 063. 4	2, 194. 5	2, 324. 8	2, 455. 2	2, 585. 9	2, 716. 7	2, 848. 6	2, 981. 1	200
	13. 7	*13. 3*	*13. 2*	*13. 1*	*13. 1*	*13. 1*	*13. 0*	*13. 1*	*13. 2*	*13. 3*	
300	1, 808. 6	1, 944. 1	2, 076. 6	2, 207. 6	2, 337. 9	2, 468. 3	2, 598. 9	2, 729. 8	2, 861. 8	2, 994. 4	300
	13. 8	*13. 3*	*13. 2*	*13. 0*	*13. 0*	*13. 1*	*13. 0*	*13. 2*	*13. 3*	*13. 4*	
400	1, 822. 4	1, 957. 4	2, 089. 8	2, 220. 6	2, 350. 9	2, 481. 4	2, 611. 9	2, 743. 0	2, 875. 1	3, 007. 8	400
	13. 7	*13. 5*	*13. 1*	*13. 1*	*13. 0*	*13. 0*	*13. 0*	*13. 1*	*13. 2*	*13. 3*	
500	1, 836. 1	1, 970. 7	2, 102. 9	2, 233. 7	2, 363. 9	2, 494. 4	2, 624. 9	2, 756. 1	2, 888. 3	3, 021. 1	500
	13. 7	*13. 3*	*13. 1*	*13. 0*	*13. 0*	*13. 1*	*13. 1*	*13. 2*	*13. 3*	*13. 3*	
600	1, 849. 8	1, 984. 0	2, 116. 0	2, 246. 7	2, 376. 9	2, 507. 5	2, 638. 0	2, 769. 3	2, 901. 6	3, 034. 4	600
	13. 6	*13. 3*	*13. 1*	*13. 0*	*13. 0*	*13. 1*	*13. 0*	*13. 1*	*13. 2*	*13. 3*	
700	1, 863. 4	1, 997. 3	2, 129. 1	2, 259. 7	2, 389. 9	2, 520. 6	2, 651. 0	2, 782. 4	2, 914. 8	3, 047. 7	700
	13. 6	*13. 3*	*13. 1*	*13. 0*	*13. 1*	*13. 0*	*13. 1*	*13. 2*	*13. 2*	*13. 3*	
800	1, 877. 0	2, 010. 6	2, 142. 2	2, 272. 7	2, 403. 0	2, 533. 6	2, 664. 1	2, 795. 6	2, 928. 0	3, 061. 0	800
	13. 5	*13. 2*	*13. 1*	*13. 0*	*13. 1*	*13. 1*	*13. 1*	*13. 2*	*13. 2*	*13. 4*	
900	1, 890. 5	2, 023. 8	2, 155. 3	2, 285. 7	2, 416. 1	2, 546. 7	2, 677. 2	2, 808. 8	2, 941. 2	3, 074. 4	900
	13. 5	*13. 2*	*13. 1*	*13. 0*	*13. 1*	*13. 0*	*13. 2*	*13. 2*	*13. 3*	*13. 3*	
1,000	1, 904. 0	2, 037. 0	2, 168. 4	2, 298. 7	2, 429. 2	2, 559. 7	2, 690. 4	2, 822. 0	2, 954. 5	3, 087. 7	1,000

WASHINGTON, December 22, 1932.

○